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EXPERIMENTAL INVESTIGATION OF THE ADSORPTION OF ORGANIC CONTAMINANTS IN WASTE WATER ON GRANULAR ACTIVATED CARBON

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CHAPTER I
INTRODUCTION

The object of this investigation was to obtain basic data concerning the removal of organic contaminants from waste water by adsorption on granular activated carbon. To this end, adsorption isotherms for the organic contaminants, classified as total organic carbon (TOC), and the activated carbon were determined. In addition, diffusion coefficients relating to both internal and pore diffusion of the organic contaminants into the carbon, were evaluated from batch kinetic data.

Activated carbon has been used in the treatment and purification of water for many years. The application of granular or powdered activated carbon in the treatment of waste water, however, has steadily gained attention during the past decade. Although early motivation for using the process with waste water centered mainly on its effectiveness in removing such biologically resistant substances as alkyl benzene sulfonates (ABS), present interest derives from the fact that the process is being seriously considered as a standard treatment step for removal of organic contaminants from waste water. Information gathered at demonstration plants at Lake Tahoe (1) and Pomona (2), with domestic waste water, and in Cincinnati (3), with domestic and industrial waste water, has established the applicability and potential usefulness of the process.

The development of reliable design criteria, clearly, must precede any large scale adoption of the carbon adsorption process in waste water treatment. The present status of knowledge on this particular problem is characterized by important gaps and considerable uncertainty, despite the fact that a very large body of information relating to adsorption in general exists. With regard to adsorption in waste water systems most of the

difficulties arise from the very nature of the waste water itself. The organic contaminant concentration of the domestic waste, usually on the order of 20 to 30 ppm in terms of TOC, is, clearly, extremely low, and the large variety of substances which comprise the organic content is both variable and virtually impossible to identify in detail. Certain classes of contaminants are objectionable as notorious pollutants if present in low concentrations. Furthermore, the waste water is usually unstable and subject to decay due to biological and other processes. Under these circumstances, it is expedient (and possibly inevitable) to express the organic contaminant content in terms of the equivalent total organic carbon. While the TOC content is, admittedly, a gross measure of organic contaminants, the method circumvents difficulties relating to the variable and unknown composition of the waste water, and also overcomes difficulties arising from its unstable nature because fast TOC determinations can be made with available instrumentation.

It is, perhaps, largely due to these difficulties that most earlier work on adsorption relates to the removal of a single organic contaminant species considered most likely to be present in waste water. Morris and Weber (4) studied the adsorption of ABS on granular carbon because this is obviously one of the possible contaminants in waste water, and together with his co-workers Weber extended these studies to a host of individual organic species (5,6). A summary of published work on this problem is presented in Table I for reference. The motivation for this type of work, i.e. the study of adsorption on carbon of individual organic contaminants, resides in the hope that the cumulative results will lead to an understanding of waste water adsorption on activated carbon.

The logical basis for this point of view is essentially sound, and, at any rate, the results are of intrinsic value without regard to whether

TABLE 1

Experimental Studies on Adsorption of Organic Substances Present in Waste Water by Activated Carbon

Investigator	System	Reference
Morris and Weber	Tetradecyl benzene sulfonate and dodecyl benzene sulfonate	Environmental Health Series, AWTR-9, USPHS
Dedrick and Beckman	2-4 Dichlorophenoxy acetic acid	Chem.Eng.Progress Series, 74, Vol. 63 (1967)
Buzzell	Phenol and its derivatives	D.Sc. Thesis (Chem.Eng.) Washington Univ. (1966) University Microfilms 66-752
Weber and Rumer	Sulfonated alkyl benzene	Water Resources Res. 1, 301 (1965)
Snoeyink	Phenols, 4 nitrophenol	Ph.D. Thesis (San. Eng.) Univ. of Michigan (1968)
Weber and Gould	2,4,5 Trichlorophenoxy-acetic acid, and other pesticides	Advances in Chemistry Series No. 60 "Organic Pesticides in the Environment"
Schwartz	2,4 dichloro phenoxy-acetic acid	Environ.Sci & Tech. 1, 333 (1967)
Digiano and Weber	Phenol, p-nitrophenol and hexabenzene sulfonate	"Mathematical Modelling of Sorption Kinetics in Finite and Infinite-Bath Systems" Res. Rep., Civil Eng. Dept., Div. of San. and Water Resources, Univ. of Michigan (1969)

or not they elucidate the very complex problems associated with the treatment of actual waste water. Nonetheless, this approach is burdened with difficulties and also uncertainties. The difficulties are mainly associated with the inordinate effort required to investigate the adsorption of individual members of the large family of organic contaminants known, or likely, to be found in waste water. The main uncertainty is that (and this perhaps is the most critical limitation to such an approach) the incomplete present status of knowledge on solution theory precludes an unequivocal generalization of the results from simple solute adsorption data to multi-solute systems.

The use of actual waste water in the adsorption studies is, therefore, both expedient and results in information directly relevant to the design of the carbon column for waste water treatment. However, implicit in this approach is the assumption that the actual multi-solute system can be treated as a single solute system, where the entire family of organic contaminants are represented by their equivalent total organic carbon content. Whether or not this type of approximation works, however, can only be tested by comparison of the results with experiment.

Most known analytical treatments of batch adsorption kinetics do not consider chemical reactions. In the present experiments on adsorption of waste water on granulated carbon in a batch system the decay of organic matter due to bacterial action is a complicating factor. In order to account for the decrease in TOC with time, and to facilitate the interpretation of the adsorption data, the effect of the chemical reaction was incorporated in the numerical solutions which were obtained. The details of the numerical analysis are presented in a companion report (7).

We present in the sections which follow a description of the experimental work, and we then proceed with discussion and interpretation of the experimental results.

CHAPTER II
EXPERIMENTAL WORK

A. Experimental System

The solid-liquid adsorption system studied in this report was comprised of granular activated carbon and waste water. The waste water was obtained directly from the Syracuse Metropolitan Waste Treatment Plant, where three types of waste water were available:

1. Screened raw waste water with an initial TOC of approximately 50 ppm.
2. Post primary treatment effluent, i.e. primary effluent followed by coagulation and chlorination, with an initial TOC of approximately 50 ppm.
3. Secondary treatment effluent with an initial TOC of approximately 20 ppm.

The first two types of waste water were obtained from the main plant of the Syracuse system, while the secondary treatment effluent was obtained from the Nine Mile Creek facility. Preliminary tests were performed on the various types of waste water, and the secondary treatment effluent was used exclusively in the batch adsorption.

The granular carbon used in our tests was manufactured by Atlas Chemical Company and marketed under the trade name Darco. Various carbons differing in size distribution were available. Narrow particle size fractions were obtained by sieving. The carbon particle size used in this work was that passing 6 mesh (0.132 in.) and retained on 8 mesh (0.093 in.). For this size fraction a mean diameter of 0.112 in. (0.28 cm) was assigned in the calculations. Physical properties provided by the manufacturer for this carbon are presented in Table 2.

TABLE 2

Properties of Granular Carbon Used in Batch Adsorption Study*

Darco Carbon Properties (Typical Values)*

Moisture Content (max., as packed)	12%
Water-solubles (determined by four leachings with boiling water)	1%
pH of Water Extract	6.0
Bulk Density (vibrating feed method), g/ml	0.39
Total Surface Area (by nitrogen adsorption), m^2/g	700
Total Pore Volume, ml/g	1.0
Mean Pore Radius, Angstroms	29
Void Space as Loaded in Plant Column	50%

*Information supplied by Atlas Chemical Industries, Inc., manufacturers of Darco carbon. Darco carbons are supplied in several size ranges; in the present work, narrow size fractions were obtained by sieving as explained in the report.

Because the concentrations involved in this work were very low, it was necessary to wash the carbon very thoroughly before use. Leachable impurities in the carbon would have a marked effect on the adsorption data as can be seen from the TOC readings following various washing and shaking cycles with water in Table 3. The procedure for washing the carbon was as follows:

1. The granular carbon sample was spread over two sieves and washed under running tap water for 24 hours.
2. Different dosages (see Table 3) of carbon were placed in a set of Erlenmeyer flasks, and to each flask 100 ml of distilled water was added. The entire set of flasks was shaken for 24 hours, and then samples of liquid were withdrawn for TOC determination. The observed TOC concentrations are shown in the third row of Table 3.
3. The water in the flasks was poured out, the carbon sample in each flask was washed with distilled water for five times.
4. After the washing 100 ml of distilled water was again added to each flask, and the 24-hour shaking cycle, followed by TOC determinations, were repeated. The observed TOC levels following this second 24-hour shaking cycle are tabulated in the last row of Table 3.
5. Upon completion of the second shaking cycle the carbon samples were washed in distilled water for five times as in (3), and then placed in the oven, at 120°C, to dry for 24 hours. These carbon samples were used in the adsorption experiments.

B. Equipment

1. Total Organic Carbon Analyzer

The TOC analyses were performed using a Beckman Model 915 Total

TABLE 3

TOC Levels Caused by Leaching of Granulated Carbon
Using 100 ml Distilled Water

(1) Flask No.	1	2	3	4	5	6	7
(2) Carbon Dosage, gm	0.065	0.135	0.239	0.349	0.548	0.698	0.860
(3) TOC after first 24-hr. shaking cycle ppm	8	9	10	11	12	13	14
(4) TOC after second 24-hr. shaking cycle ppm	3	4	4	3	3	3	3

(1) Flask No.	8	9	10	11	12	14
(2) Carbon Dosage, gm	1.016	1.535	2.993	5.762	9.990	22.111
(3) TOC after first 24-hr. shaking cycle ppm	6	7	8	7	12	20
(4) TOC after second 24-hr. shaking cycle ppm	3	3	3	4	4	4

Organic Carbon Analyzer with a Model 215 A Infrared Analyzer. The instrument was originally developed by the Dow Chemical Company expressly for waste water analysis. It can be used to determine the total carbon content and the inorganic carbon in the test sample, and the TOC is obtained by taking the difference of these two measurements.

The main instrument has two combustion tubes. The total carbon content is determined by injecting a small carefully measured sample (20-30 µℓ) using a Hamilton SK148 50 syringe into the high temperature combustion tube. The temperature in this combustion tube is 950°C and it is packed with a catalyst impregnated on Asbestos fiber. Under these conditions all of the carbon, both organic and inorganic, is oxidized to CO_2. The resulting products are then swept through by the carrier gas into the infrared analyzer for determination of CO_2 content. The carrier gas flow through both combustion tubes is maintained at a steady rate throughout the entire duration of operation of the instrument, and it serves to supply the oxygen necessary for combustion, to prevent the combustion tubes from overheating and cracking, and to sweep the combustion products into the infrared analyzer. For the carrier gas in our experiments we used bottled compressed air with negligible impurities. Because the carrier gas flow must be maintained until the temperatures in the combustion tubes return to room temperature, after the analyzer is turned off, the consumption of gas is somewhat high.

The inorganic carbon content is determined in a similar way but the combustion tube for this determination is heated to only 150°C and the catalyst is composed of quartz chips wetted with 85% phosphoric acid. Under these conditions only the inorganic carbon

(i.e. CO_3^{--}, etc.) is converted to CO_2.

Attempts were made to follow the COD concentration history in our adsorption experiments. The COD measurements were made with a Delta Scientific Model 260 Photometric Analyzer. However, the analytical procedure is tedious and time-consuming. Inasmuch as the waste water is susceptible to decay by bacterial action, this particular analytical procedure seemed quite unsuitable. Consequently, COD determinations were abandoned in favor of TOC measurements.

2. Water Bath and Shaker

The adsorption experiments entailed following the TOC concentration history of a fixed volume of waste water contacted with varying dosages of granular carbon at constant temperature. A WCLID Model 2156 water bath shaker was used for temperature control and mixing. This constant temperature bath had a range of 25-120°C with an accuracy of ± 0.5°C, and a variable speed (and stroke length) reciprocating shaking action. The shaking action was required to insure good mixing, thereby eliminating effects of liquid phase resistance in the adsorption studies. Poor mixing would, of course, introduce considerable uncertainties in the interpretation of the data.

C. Experimental Procedure

1. Preparation of the TOC Analyzer

Repeated injections of test samples in the high temperature combustion tube tended to loosen the catalyst packing, and some of this was swept into the condenser tube. Under these conditions reproducible readings could not be obtained. In addition, leaks in the combustion tube resulted in broad peaks in the recorder traces

instead of the desired sharp peaks. Generally, the following steps were followed to get the TOC Analyzer ready:

(a) Check leaks and the catalyst packing in the high temperature combustion tube. If a sufficient quantity of catalyst had been swept out of the tube, the combustion chamber was cleaned and repacked with fresh catalyst. Catalyst preparation and packing procedure are described in the Beckman instruction manual.

(b) Check the compressed air supply.

(c) Check the ink supply system of the recorder.

(d) Check the zero point adjustment to insure zero adjustment which can be made for both inorganic and total carbon channels with only carrier gas flowing. Otherwise, adjustments in the Infrared Analyzer should be made as described in the instruction manual.

(e) Allow the Analyzer to warm up. This requires about one hour.

It is, of course, imperative that the instrument remain in a satisfactory operating condition throughout the entire period of a given kinetic experiment. Therefore, the foregoing procedure was necessary.

2. Preparation of Standard Solutions

Aqueous solutions of potassium biphthalate ($KHC_8H_4O_4$) were made up for the organic carbon standard, and sodium carbonate and bicarbonate (Na_2CO_3 and $NaHCO_3$) solutions were prepared for the inorganic carbon standards. All standard solutions were prepared with CO_2-free distilled water, which was obtained by boiling distilled water for 30 minutes. These solutions were stored in carefully

cleaned glassware and protected from atmospheric CO_2 by means of CO_2-absorbent traps. All glassware used in our experiments was thoroughly washed using cleaning solution.

3. Waste Water Decay Study

The rates of decay of organic contaminants in raw waste water, primary treatment, and secondary treatment effluents were studied by determining the TOC concentration history. This was done by placing the waste water in a 4000 ml flask with a magnetic stirrer to keep the sample mixed and at uniform temperature, which was held constant by placing the flask in a constant temperature bath. Samples were withdrawn periodically for TOC analysis. It was observed that the TOC level approached a constant value in approximately two weeks.

4. Adsorption Study

In the adsorption work only secondary treatment effluent was used. The waste water was first filtered for removal of suspended matter, and then 100-ml quantities were added to different dosages of granular carbon placed in a set of fourteen 250-ml Erlenmeyer flasks. A measurement of the initial TOC concentration of the liquid was made. The entire set of flasks was placed in the constant temperature bath and shaken continuously at high speed. The TOC concentration history was studied according to the following procedure:

(a) One flask was removed from the bath and the time was recorded.

(b) A 10-ml sample of liquid was withdrawn using a pipet. This sample was filtered under reduced pressure, and microliter samples were withdrawn, using a Hamilton SK148 50 syringe, for immediate TOC analysis.

(c) The remainder of the filtrate was returned to the flask, and the flask was replaced into the temperature bath.

(d) Steps (a) - (c) were repeated with each of the remaining flasks. This cycle was repeated periodically until equilibrium was attained.

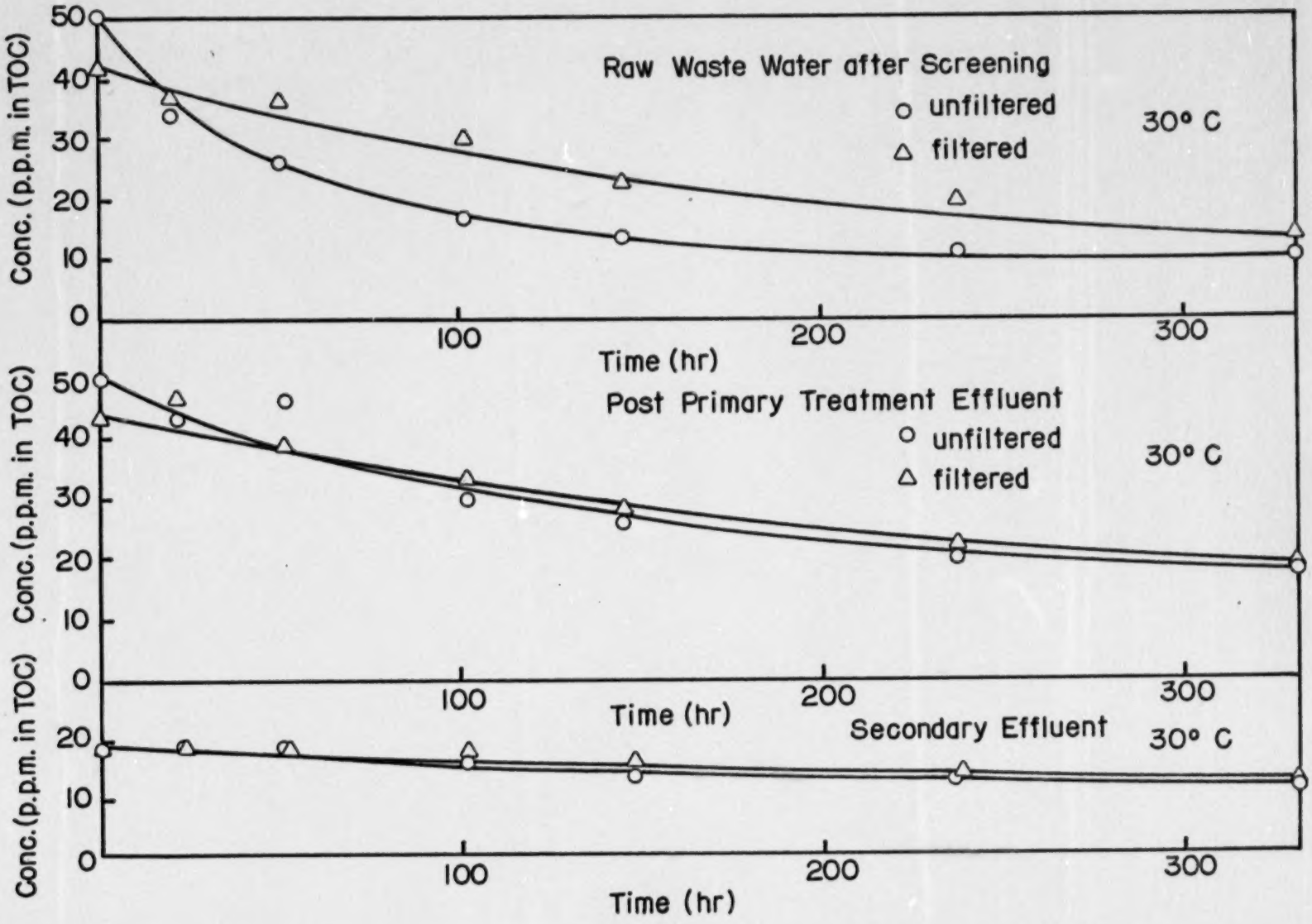

Fig. 1 Observed Organic Contaminant Concentration History

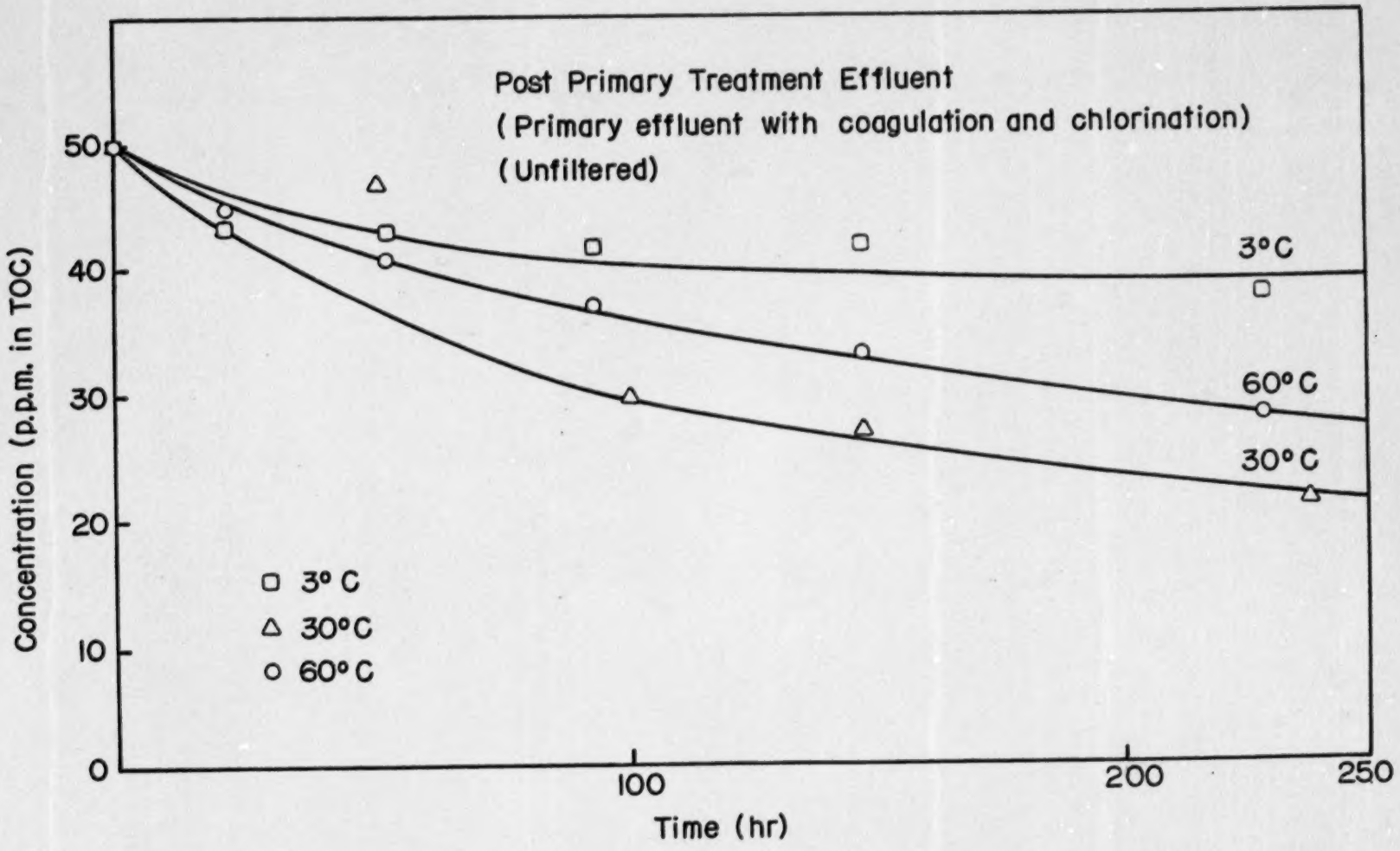

Fig. 2 Observed Dependence of Concentration History on Temperature

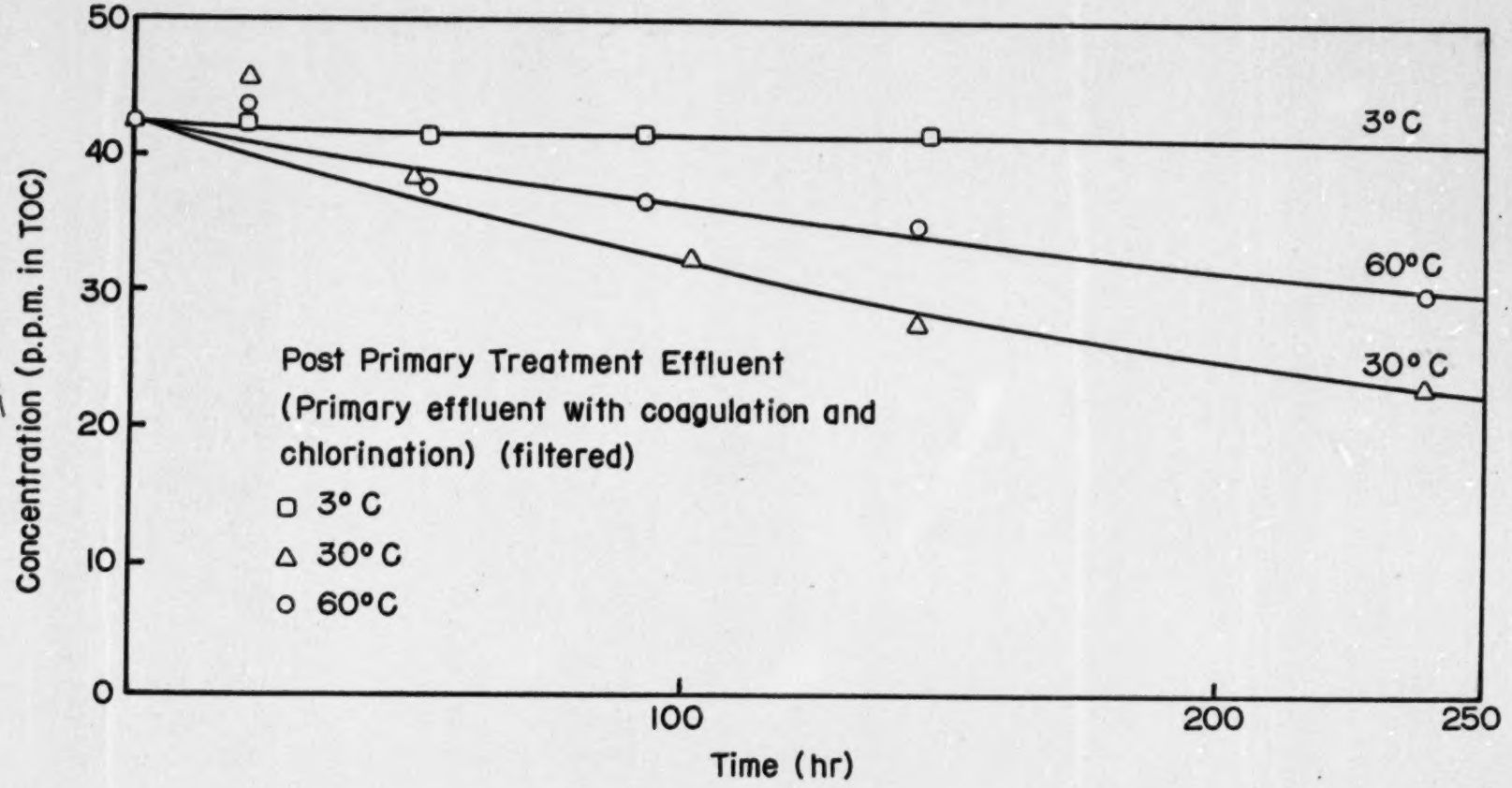

Fig. 3 Observed Dependence of Concentration History on Temperature

CHAPTER III
EXPERIMENTAL RESULTS

A. Waste Water Decay

The concentration history of dissolved organic matter for the three classes of waste water over a span of two weeks is shown in Figures 1 to 4 for three different temperatures. A significant feature of these data is that the rate of decay did not vary monotomically with temperature. Explanations for this observed behavior will be given in a later section of this report.

The rate of decay data of organic contaminants in the secondary treatment effluent at 30°C was fitted to the kinetic equation

$$\bar{R} = \frac{dC}{dt} = - k \, (C - C_{B_E})^n \qquad (1)$$

in which C is the TOC concentration in ppm, and C_{B_E} is the asymptotic value of TOC at large time obtained from the experiment. For n=1 the value of the rate constant k was found to be 6.25×10^{-3} hr.$^{-1}$ (see Figure 4). This value of the rate constant was used in the evaluation of the diffusion coefficients. The rate equation (1) is used as a convenient aid in the proper calibration of the adsorption isotherm and evaluation of the diffusion coefficients, and is merely an expression for curve-fitting the experimental observations.

B. Adsorption Isotherm

Using the batch adsorption studies, the adsorption isotherm data are obtained from the asymptotic value of the concentration at large times, i.e. when no further decrease in the concentration of the liquid phase occurs. Under these conditions, the liquid and solid phases are assumed to be in equilibrium, and the concentrations in the two phases are designated by C_E

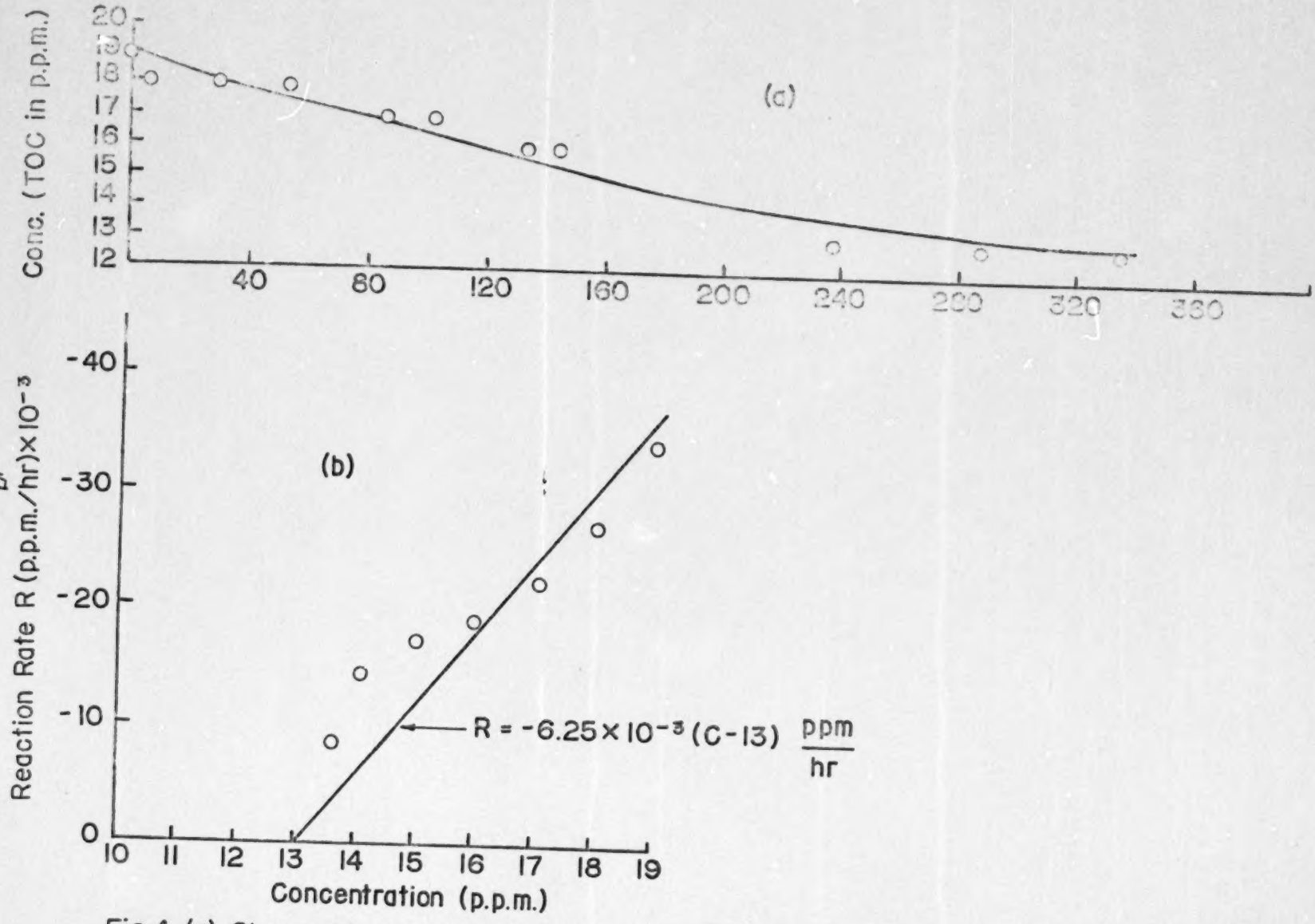

Fig. 4 (a) Observed Concentration History for Secondary Treatment Effluent at 30° C
(b) Decay Rate - Concentration Dependence for Data of Fig. 4 (a)

and q_E, respectively. These concentrations are related by the material balance

$$Mq_E + VC_E - V \int_o^{t_E} \bar{R}\, dt = VC_o \qquad (2)$$

or

$$q_E = \frac{V}{M} (C_o - C_E) + \frac{V}{M} \int_o^{t_E} \bar{R}\, dt \qquad (3)$$

The ratio (M/V) is the carbon dosage and C_o is the initial concentration of TOC. The equilibrium concentrations of TOC in the liquid phase, C_E, are shown in Table 4 together with the corresponding values of (M/V). These results were evaluated from the batch adsorption experiments.

In order to determine q_E using equation (3) the integral $\int_o^{t_E} \bar{R}\, dt$, which accounts for organic contaminant decay, must be calculated. Using the concentration history data (C vs t), from the decay kinetics experiments, the rate R is determined as a function of C as shown in Figure 4. C vs t and R vs C results are used to calculate $\int_o^{t_E} \bar{R}\, dt$ numerically for each of the batch adsorption experiments corresponding to the various carbon dosages. These results are then used to calculate q_E as shown in Table 4.

The adsorption data were represented by a Freundlich type of adsorption isotherm. This was done by plotting q_E vs C_E on log-log scales, as shown in Figure 5, and determining the best straight line through the points. The adsorption data at 30°C can be represented by the equation

$$q_E = 1.65 \times 10^{16}\, C_E^{3.68} \quad \text{at } 30°C \qquad (4)$$

in which q_E is expressed as gram organic carbon per gram of activated carbon, and C_E is expressed as gram organic carbon per cc waste water. The adsorption isotherm is strictly applicable at 30°C.

C. Adsorption Kinetics

The batch adsorption experiments were conducted at 30°C using filtered

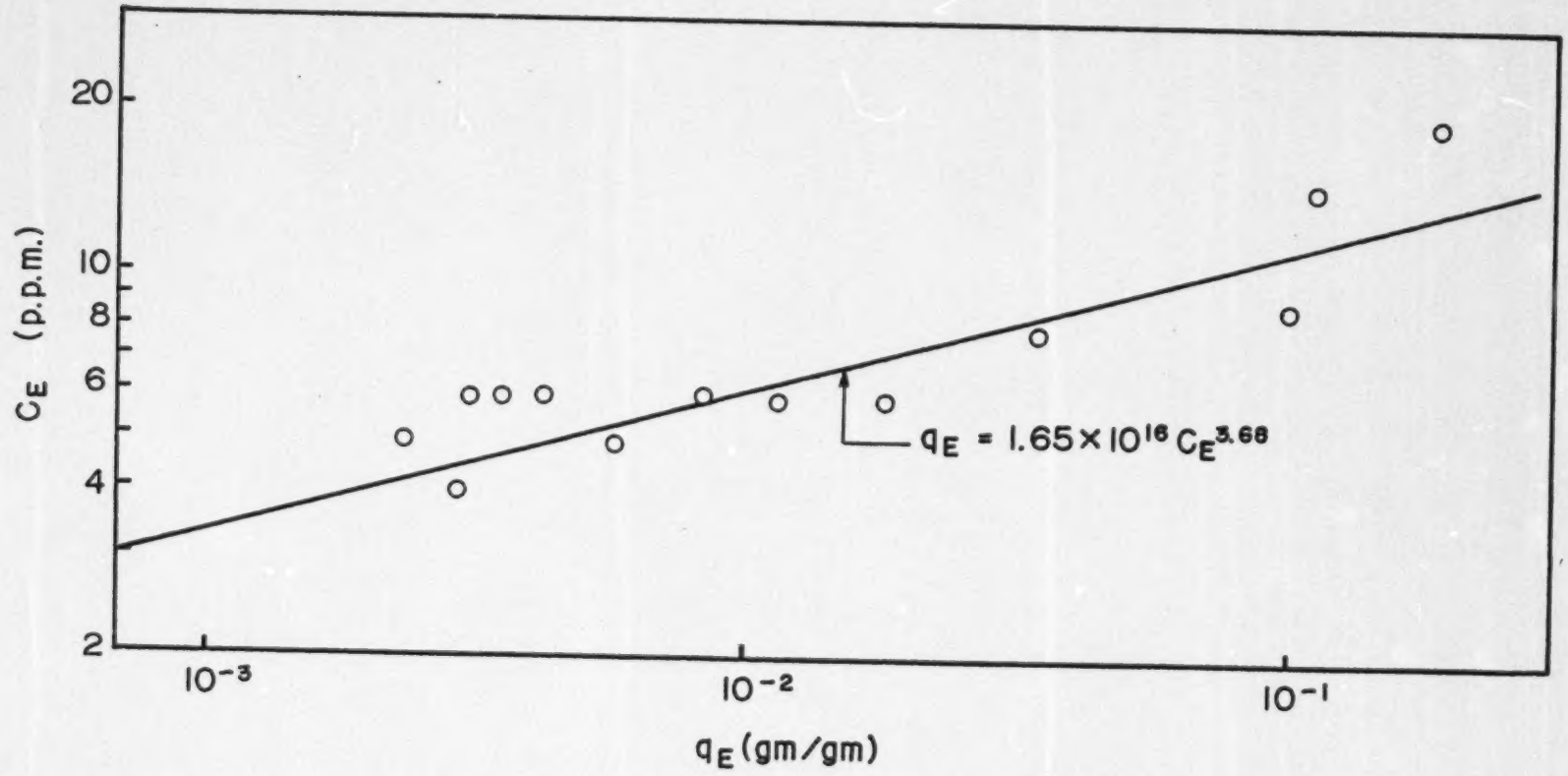

Fig. 5 Adsorption Isotherm for Secondary Treatment Effluent at 30°C
Decay Rate Given by Eq. (1)

TABLE 4

Calculated Values for Adsorption Isotherm at 30°C -
Blank Waste Water Decay Rate Assumed to Depend on Concentration Only

No. of Flask	1	2	3	4	5	6	7
Carbon Dosage(gm)	0.003	0.006	0.009	0.030	0.070	0.110	0.152
C_E(p.p.m.)	12	11	9	8	6	6	6
$-\int_o^{t_E} Rdt$ (p.p.m.)	1.5	1.4	1.0	0.6	0.4	0.2	0.1
$C_o-C_E+\int_o^{t_E} Rdt$	5.5	6.6	9	10.4	12.6	12.8	12.9
$q_E \times 10^{-6}$ (g/g)	183,333	110,000	100,000	34,667	18,000	11,636	8,486

No. of Flask	8	9	10	11	12	14	1,
Carbon Dosage(gm)	0.240	0.308	0.412	0.516	0.584	Blank	(3700 ml) 13.502
C_E(p.p.m.)	5	6	6	4	5	13	6
$-\int_o^{t_E} Rdt$ (p.p.m.)	0.1	0	0	0	0		0.1
$C_o-C_E+\int_o^{t_E} Rdt$	13.9	13	13	15	14		12.9
$q_E \times 10^{-6}$ (g/g)	5,792	4,220	3,155	2,907	2,397		3,535

TABLE 5

Experimental Concentration Histories in Batch Adsorption

Waste Water: Filtered Secondary Treatment Effluent
Volume Liquid: 100 ml
Temperature: 30°C
Carbon: Darco granular carbon - 6/8 mesh size

Concentrations expressed in p.p.m. TOC

Flask No. 1 - Weight Carbon: 0.003 gm

Time (hr.)	0	3	8	15	30	54	87	110	133	208	288
Conc. (p.p.m.)	19	18	17	16	17	16	15	14	12	12	12

Flask No. 2 - Weight Carbon: 0.006 gm

Time (hr.)	0	3	8	15	30	54	87	110	133	208	288
Conc. (p.p.m.)	19	18	17	16	17	16	14	14	10	11	12

Flask No. 3 - Weight Carbon: 0.009 gm

Time (hr.)	0	3	8	15	30	54	87	102	133	207	287
Conc. (p.p.m.)	19	17	16	16	16	15	14	13	9	9	10

Flask No. 4 - Weight Carbon: 0.030 gm

Time (hr.)	0	3	8	15	30	54	87	102	133	208	287
Conc. (p.p.m.)	19	16	15	14	14	13	12	11	8	7	8

Flask No. 5 - Weight Carbon: 0.070 gm

Time (hr.)	0	3	8	15	30	54	87	102	133	207	287
Conc. (p.p.m.)	19	14	13	13	12	12	11	10	6	6	6

Flask No. 6 - Weight Carbon: 0.110 gm

Time (hr.)	0	3	8	15	30	53	86	101	132	207	287
Conc. (p.p.m.)	19	13	12	11	10	9	9	8	7	6	6

(Continued)

TABLE 5 (Cont'd.)

Experimental Concentration Histories in Batch Adsorption

Flask No. 7 - Weight Carbon: 0.152 gm

Time (hr.)	0	3	8	15	30	53	86	101	132	207	287
Conc. (p.p.m.	19	13	11	10	9	8	8	7	7	6	6

Flask No. 8 - Weight Carbon: 0.240 gm

Time (hr.)	0	2	7	14	29	53	86	101	132	207	287
Conc. (p.p.m.)	19	13	11	9	8	7	7	7	7	5	5

Flask No. 9 - Weight Carbon: 0.308 gm

Time (hr.)	0	2	7	14	30	53	86	101	132	207	287
Conc. (p.p.m.)	19	12	10	10	8	7	7	6	6	5	6

Flask No. 10 - Weight Carbon: 0.412 gm

Time (hr.)	0	2	7	14	29	53	86	101	132	207	287
Conc. (p.p.m.)	19	12	11	10	8	7	6	6	6	7	6

Flask No. 11 - Weight Carbon: 0.516 gm

Time (hr.)	0	2	7	14	29	53	86	101	132	206	284
Conc. (p.p.m.)	19	11	9	9	8	9	8	5	5	4	4

Flask No. 12 - Weight Carbon: 0.584 gm

Time (hr.)	0	2	7	14	29	53	86	101	132	206	287
Conc. (p.p.m.)	19	11	11	9	7	7	6	4	4	6	5

Flask No. 14 - Blank Waste Water

Time (hr.)	0	8	30	53	86	102	133	144	237	287	334
Conc. (p.p.m.)	19	18	18	18	17	17	16	16	13	13	13

(Continued)

TABLE 5 (Cont'd.)

Experimental Concentration Histories in Batch Adsorption

Flask No. 15 - Weight Carbon: 13.502 gm*											
Time (hr.)	0	2	7	14	29	53	86	109	132	207	287
Conc. (p.p.m.)	19	12	11	9	9	6	7	6	7	5	6

*The waste water sample size for Flask No. 15 was 3700 ml. For all other flasks the sample size used was 100 ml.

secondary effluent. Fourteen granular carbon dosages were used ranging from a dosage of 0.003 g carbon/100 ml waste water to 0.584 g carbon/100 ml waste water. Approximately 270 hours were required to complete the experiments. The results of these experiments are shown in Table 5 and also presented graphically in Figures 6 to 10.

The measured concentration history can, in principle, be used to calculate physical parameters characterizing the adsorption process by comparison with the results of theoretical calculations. The theoretical results will depend upon the assumption of the rate-controlling mechanism which must be specified a priori. The strong agitation used in the present experiments eliminates the need to consider liquid phase resistance, and, consequently, the liquid concentration at the surface of the carbon can be assumed to be the same as that of the bulk solution. Thus, the diffusion process within the carbon is the rate-controlling step. We shall consider the experimental results in terms of the following particular models:

1. Internal Diffusion Model

The adsorbent is assumed to behave like a homogeneous body and the diffusion process is taken to be analogous to solid diffusion. The assumption of negligible liquid side resistance permits us to invoke an equilibrium condition at the solid-liquid interface, i.e. at the solid-liquid interface the solid and liquid concentrations are related by the adsorption isotherm.

2. Pore Diffusion Model

The adsorption is assumed to be controlled by the diffusion of adsorbate through the liquid filling the pores of the adsorbent. At any point within the adsorbent the concentration of the liquid in the pore space is assumed to be in equilibrium with that of the solid matrix.

The experimental data are interpreted in terms of these two models which permit evaluation of the internal or pore diffusion coefficient. Physically, the pore diffusion model appears to be more realistic, although the choice of model must ultimately depend upon the degree of agreement between experimental and theoretical results and, unavoidably to some extent, upon the complexity of the calculations required in each case.

The batch adsorption process for a system obeying the Freundlich type adsorption isotherm and including chemical reaction in the liquid phase was analyzed numerically. The details of the numerical analysis are presented in a companion report and will not be repeated here. We present here a brief outline of the procedure used in determining the different values of the coefficients.

1. Evaluation of the Internal Diffusion Coefficient

The results of the numerical calculations provide the concentration history in dimensionless variables, $\alpha = (MA/V)^{1/a-1} C$ vs $\theta = 4\pi Dt/R^2$, for specified sets of values of the following parameters:

(a) adsorption isotherm exponent, a,

(b) dimensionless concentration, $\alpha_o = (MA/V)^{1/a-1} C_o$,

(c) dimensionless chemical reaction parameter, $\delta = kR^2/4\pi D$ for the chemical reaction of the type given by equation (1).

The symbol (M/V) designates the carbon dosage, C_o is the initial waste water concentration, D the internal diffusion coefficient, R the average carbon particle radius, and A and a are the coefficient and exponent, respectively, in the adsorption isotherm (see equation 4).

The parameters α_o and a are determined from the experimental conditions and the results of the supplementary rate of decay experiments which were carried out. The chemical reaction parameter δ

contains the diffusion coefficient D, which is the unknown to be determined. Fortunately, it is found that the α vs θ relationship is not very sensitive to variations in the value of δ so long as the value assumed is of the correct order of magnitude. The actual procedure used here for the evaluation of D was the following:

From experiments the liquid phase concentration, C, at a given time, t, was known. The ratio C/C_o, which is equal to α/α_o, was computed. From the theoretical curve the value of θ corresponding to this particular value of α/α_o was determined. Using the definition of θ the diffusion coefficient was calculated according to the equation

$$D = \frac{\theta \cdot R^2}{4\pi t} \qquad (5)$$

A summary of these results is presented in Table 6, with more detailed data to be found in Appendix I.

If greater accuracy in the determination of D is desired, and is indeed warranted, an iterative procedure can be used. An obvious procedure would entail using a trial value of D to determine δ, and from this and the theoretical concentration curve one calculates the diffusion coefficient D. If the comparison between the trial and the calculated values of D is not satisfactory, a second estimate for δ based on the calculated value of D is used. The procedure is repeated until the desired degree of agreement between trial and calculated values is attained.

2. Evaluation of Pore Diffusion Coefficient

For this model the parameters which describe the adsorption process are:

$$\alpha_o = \left(A \frac{\rho}{B}\right)^{1/(a-1)} C_o \; ; \; \Phi_1 = \frac{3M}{V_p} \varepsilon \; ; \; \Phi_2 = \frac{\varepsilon R^2 K}{D_p} \left(\frac{\varepsilon}{A\rho}\right)^{(n-1)/(a-1)} \qquad (6)$$

These values can be determined from knowledge of the experimental conditions. The values of ε and ρ are estimated to be equal to 0.5 and 0.39 gm/cm^3, respectively.

The theoretical concentration history, $(A \frac{\rho}{E})^{1/(a-1)} C$ vs $(\frac{D_p}{\varepsilon R^2})t$ can be generated for the specified parameter values. The pore diffusion coefficient D_p is determined by comparing the theoretical and experimental results in a manner similar to the one described above. Table 7 contains a summary of these results. More detailed results are presented in Appendix II.

TABLE 6

Internal Diffusion Coefficients from Batch Adsorption Data

Flask No.	Carbon Dosage (g/cc)	Value of D_{eff} (cm^2/sec.)
(1)	3×10^{-5}	$3.2 \sim 3.5 \times 10^{-9}$
(3)	9×10^{-5}	$3.2 \sim 8.2 \times 10^{-9}$
(4)	3×10^{-4}	$2.6 \sim 8.4 \times 10^{-9}$
(5)	7×10^{-4}	$3.2 \sim 6.3 \times 10^{-9}$
(6)	1.1×10^{-3}	$3.5 \sim 19 \times 10^{-9}$
(7)	1.52×10^{-3}	$2.2 \sim 26 \times 10^{-9}$
(8)	2.4×10^{-3}	$2.4 \sim 15 \times 10^{-9}$
(11)	5.16×10^{-3}	$1.9 \sim 8.0 \times 10^{-9}$
(12)	5.84×10^{-2}	$3.6 \sim 12 \times 10^{-9}$
(15)	3.67×10^{-3}	$1.6 \sim 8.2 \times 10^{-9}$

TABLE 7

Pore Diffusion Coefficients from Batch Adsorption Data

Flask No.	Carbon Dosage (g/cc)	Value of D_{pore} (cm^2/sec.)
(1)	3×10^{-5}	$3.4 \sim 4.3 \times 10^{-9}$
(2)	6×10^{-3}	$4.3 \sim 6.1 \times 10^{-9}$
(3)	9×10^{-3}	$4.2 \sim 16.3 \times 10^{-9}$
(4)	3×10^{-4}	$1.7 \sim 2.2 \times 10^{-8}$
(5)	7×10^{-4}	$4.0 \sim 5.1 \times 10^{-8}$
(6)	1.1×10^{-3}	$7.3 \sim 16.3 \times 10^{-8}$
(7)	1.52×10^{-3}	$6.3 \sim 9.9 \times 10^{-8}$
(8)	2.4×10^{-3}	$4.4 \sim 11.4 \times 10^{-8}$

CHAPTER IV
DISCUSSION

A. Waste Water Decay

The waste water decay effect, per se, is unimportant in the operation of the carbon adsorption column for tertiary waste treatment. It is, however, of first rank importance in the interpretation and evaluation of the batch adsorption data used to calculate the adsorption isotherm and diffusion coefficients. The waste water decay data were represented, in the present work, by a modified first order rate equation. This type of rate expression embodies the implicit assumption that the effect of the bacterial population in the waste water is unimportant. The inadequacy of this assumption is clearly demonstrated by the fact that the rate of decay is not a monotonic function of temperature (see Figures 1-3). The observed rate of decay first increases with increasing temperature and then decreases with further increase in temperature. This seems to suggest an adverse effect of high temperature on the bacterial population, and also the need to include this effect in the description of the waste water decay phenomenon. Accordingly, it might prove useful, in future work, to attempt correlation of the decay phenomenon relative to BOD measurements over 21 day periods. Instead of the modified first order expression in equation (1), one might take the rate of decomposition as a function of time, which is tantamount to assuming that the rate of decay is solely determined by the bacterial population, and, therefore, dependent on temperature as well as time. Attempts were made to analyze the data within this framework, but the results turned out to be less satisfactory as will be explained later.

B. Adsorption Isotherm

The data used to define the adsorption isotherm line exhibit

considerable scatter as shown in Figure 5. No doubt this can be attributed largely to the complex nature of the waste water, and the limitations inherent in treating this multi-solute system as a pseudo single-solute solution. In addition, however, the method of evaluating the term $\int_o^\infty \bar{R}\, dt$ in equation (2) could very well contribute markedly to this scatter. The waste water decay rate was assumed to be a function of contaminant concentration only. That the decay rate is a function of time only, at a given temperature, is entirely possible, particularly if the bacterial population is the controlling factor in the decay process. Under these circumstances, the integral $\int_o^\infty \bar{R}\, dt$ can be evaluated directly from the waste water decay data. For in this case, at any given temperature,

$$\int_o^\infty \bar{R}\, dt = C_o - C_{B_E} \tag{7}$$

where C_{B_E} is the equilibrium concentration (final) of the blank waste water (see Figures 1-3). The equilibrium concentrations q_E and C_E in the solid and liquid phases, respectively, are given by

$$q_E = \frac{V}{M}\,(C_{B_E} - C_E) \tag{8}$$

The adsorption isotherm based upon this alternative expression of the decay rate is shown in Figure 11. The least squares fit of this line gives the expression

$$q_E = 1.55 \times 10^{18}\, C_E^{3.93} \tag{9}$$

It is interesting to note that the exponents for both cases of decay rate mechanism [equations (4) and (9)] are essentially the same, 3.68 and 3.93, even though the coefficients differ by two orders of magnitude. Furthermore, the scatter in Figure 11 is considerably more pronounced than that in Figure 5. This is the reason for using equation (4), in preference to equation (9), for calculation of the diffusion coefficient.

C. Diffusion Coefficients

The internal diffusion coefficient evaluated from the batch adsorption data varied between 2×10^{-9} and 2.6×10^{-8} cm^2/sec. The pore diffusion coefficients ranged between 1.5×10^{-9} and 1.63×10^{-7}, with the bulk of the values falling in the 10^{-8} cm^2/sec. range. Whereas, the significant variations in these values may suggest that the models used are inadequate, it seems more plausible to attribute these variations to a number of possible sources of error. Primary among these are errors arising from the method used to account for the waste water decay effect, those arising from the particular form of the adsorption isotherm used to generate the theoretical concentration history curves, and experimental errors associated with the TOC measurements. This last source of error is perhaps the most important one. The method used for TOC measurements is accurate within ± 1 ppm with an attendant error of approximately ± 0.05 in the value of α/α_o. The corresponding error in θ, however, could be quite considerable because of the slow adsorption encountered in most cases. The variations of the diffusion coefficients do not show any trends. Plots of D against α_o (which represents carbon dosage) for internal diffusion, and D_p against ϕ_1 for pore diffusion are shown in Figures 12 and 13, respectively, and they demonstrate this fact quite clearly. We are, therefore, inclined to view this rather large scatter in the results as essentially inevitable. The difficulties reside mainly in the complex nature of waste water and the limitations of present tools and knowledge. In the case of internal diffusion, values of D between 2.0×10^{-9} and 1×10^{-8} cm^2/sec. can tentatively be used in preliminary design calculations.

The variation in values of the pore diffusion coefficients is, clearly, so pronounced as to preclude their use in design calculations. This is quite surprising in view of the fact that the pore diffusion model

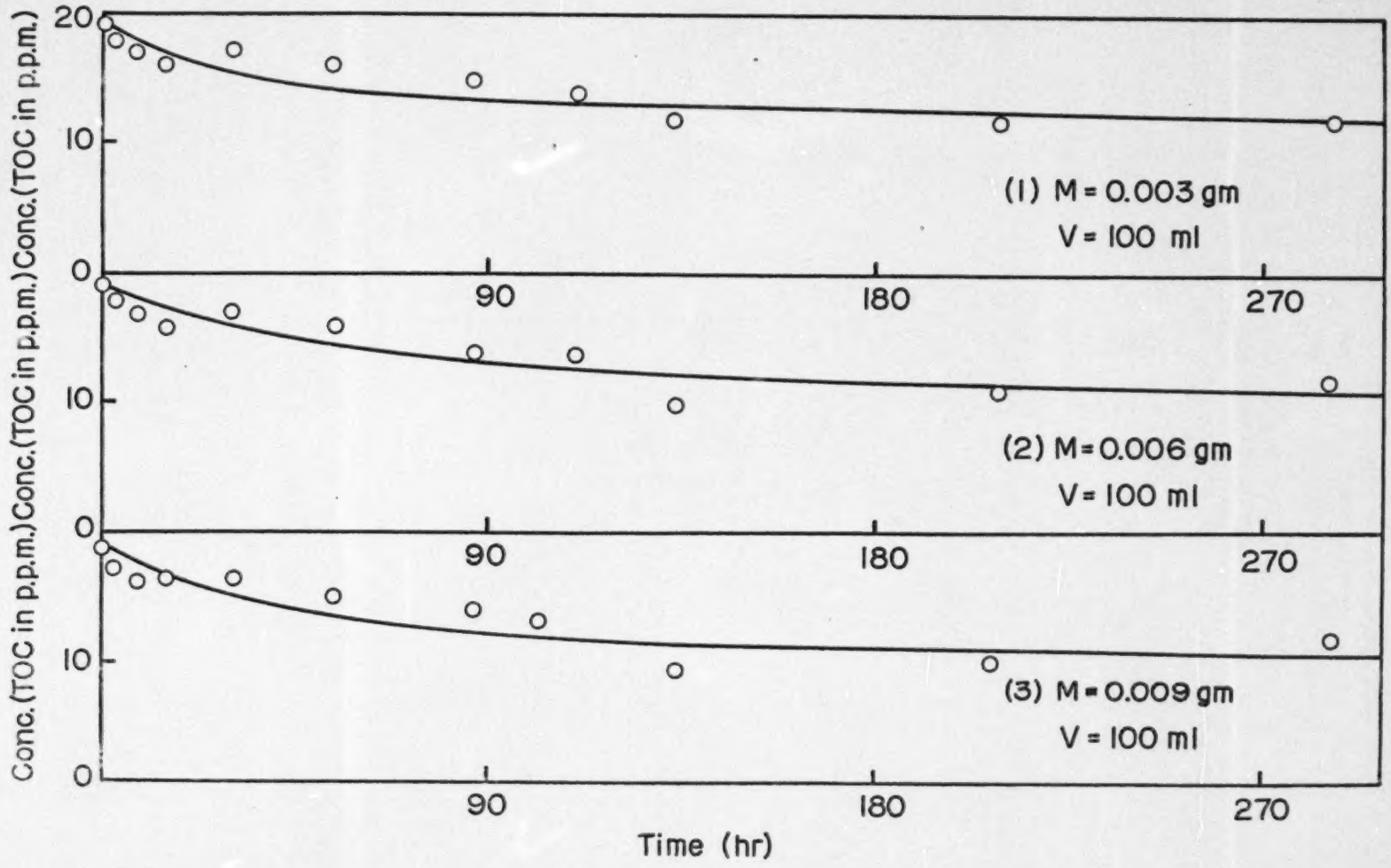

Fig. 6 Batch Adsorption Kinetics Data (a)

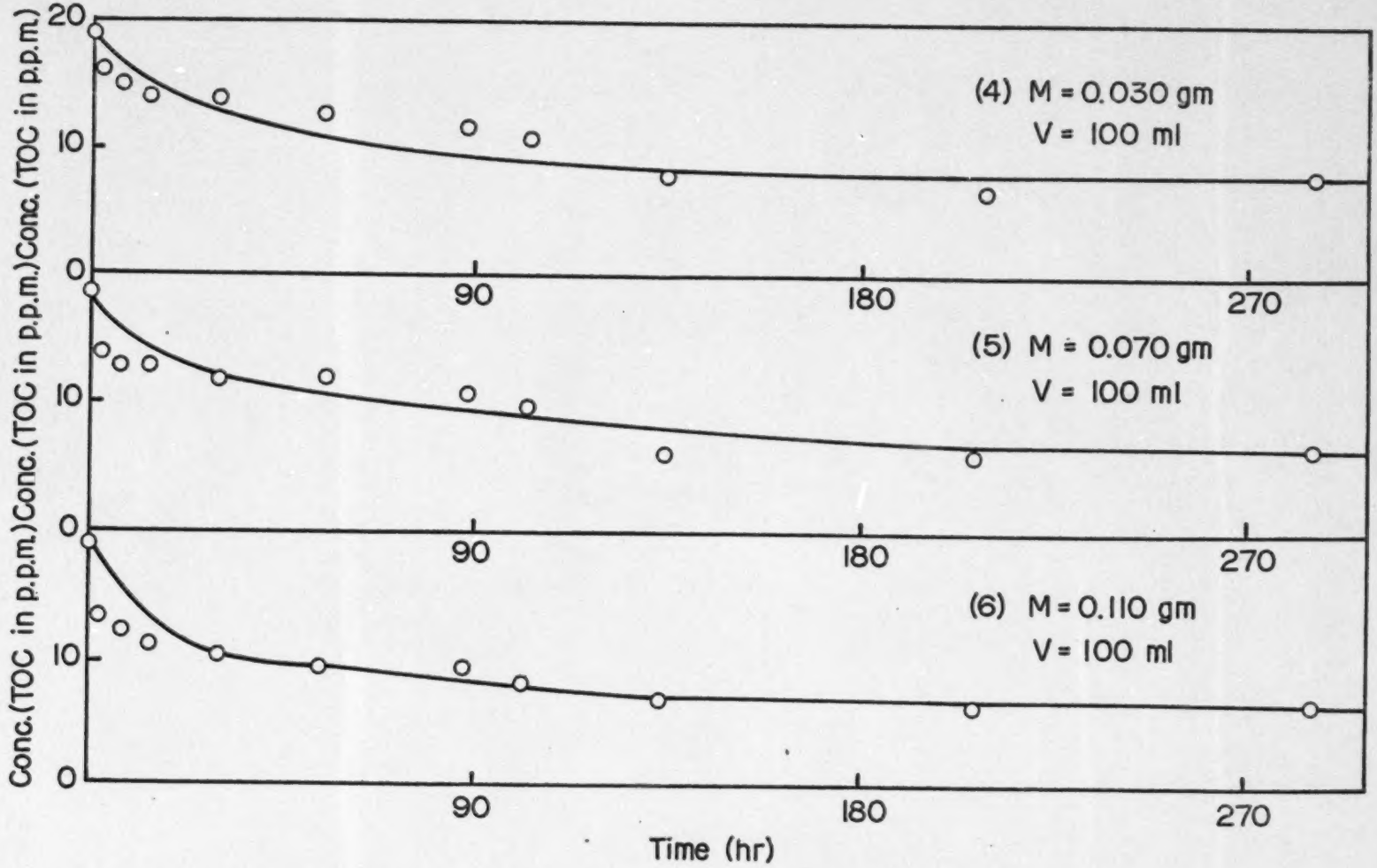

Fig. 7 Batch Adsorption Kinetics Data (b)

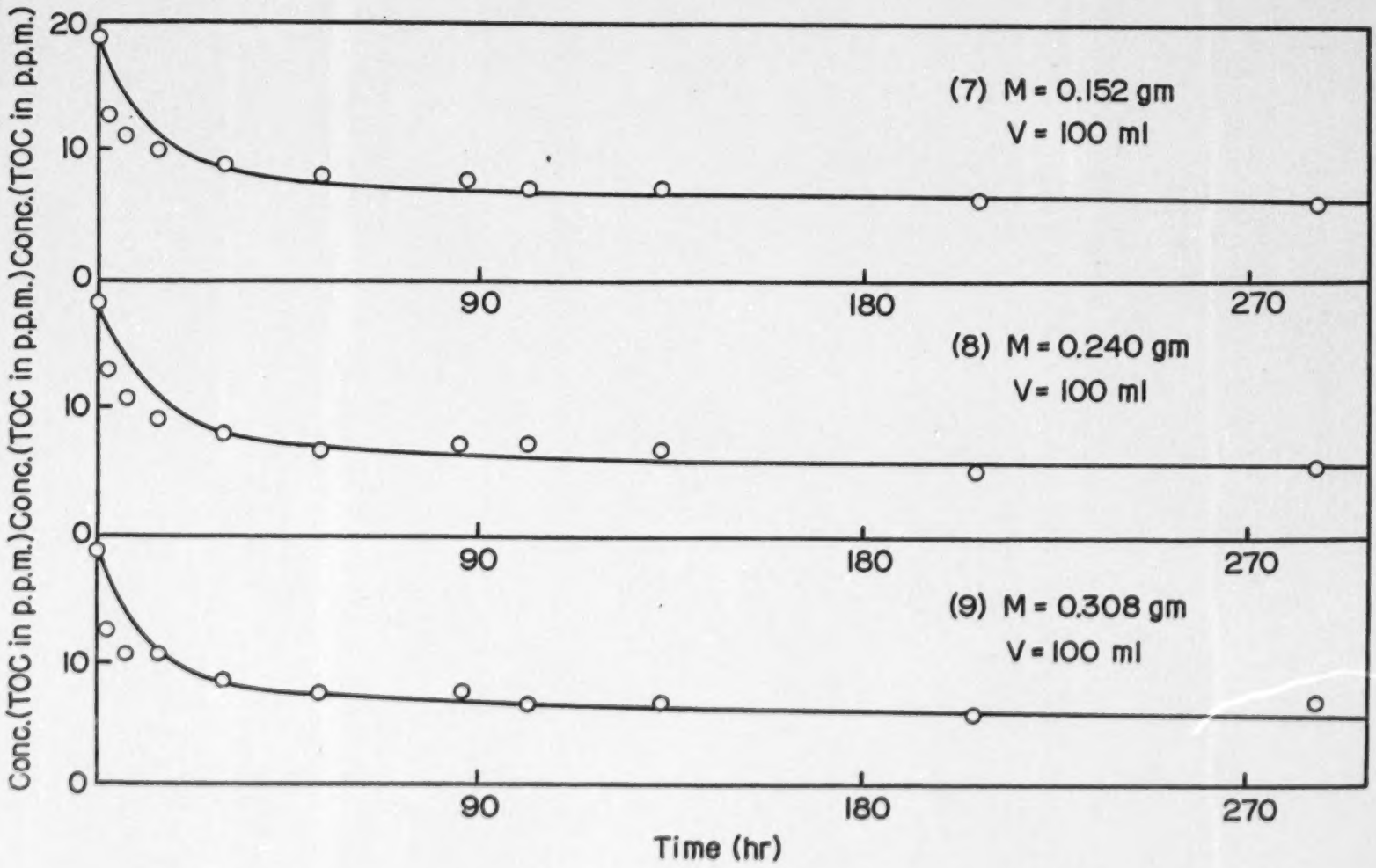

Fig. 8 Batch Adsorption Kinetics Data (c)

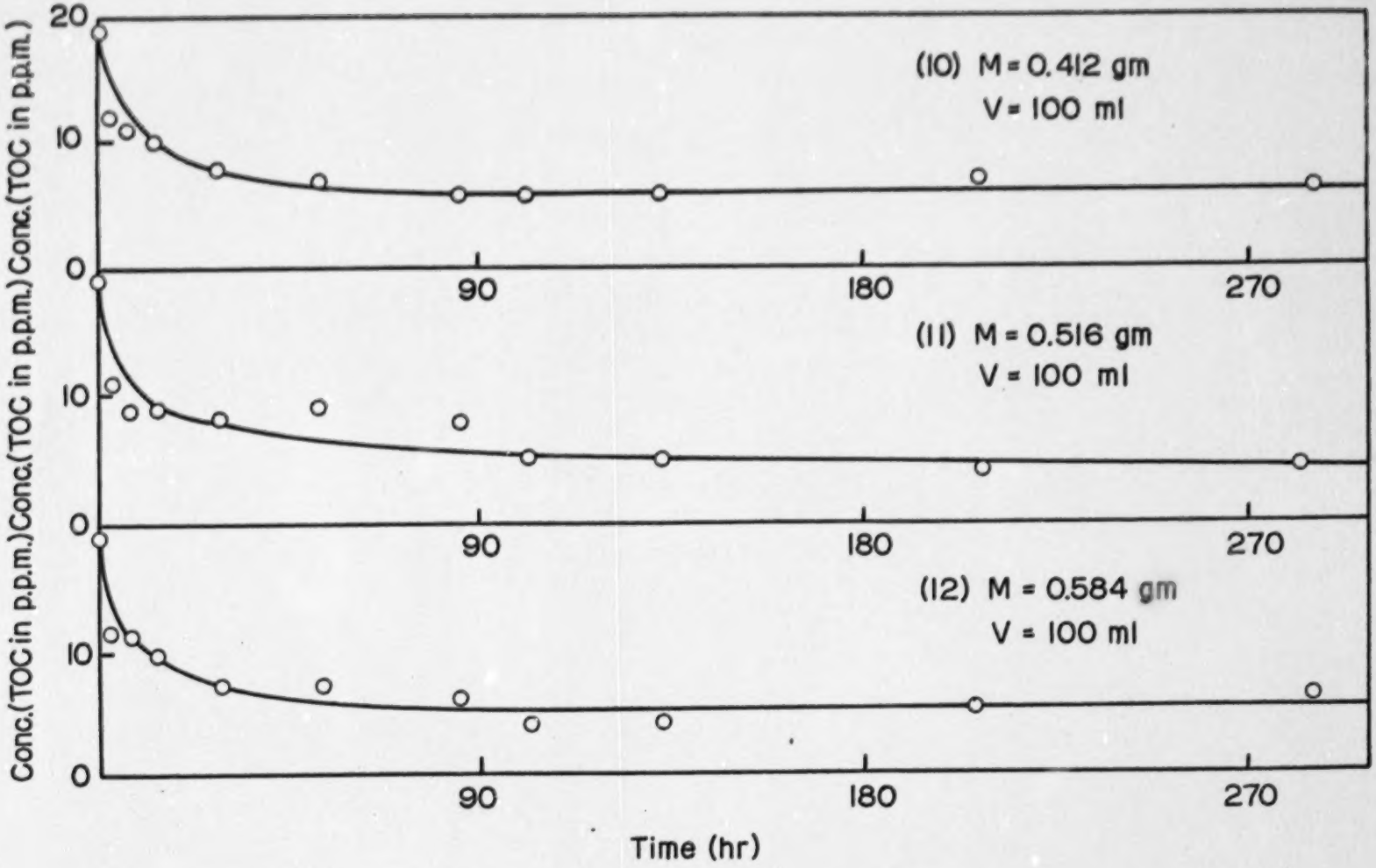

Fig. 9 Batch Adsorption Kinetics Data (d)

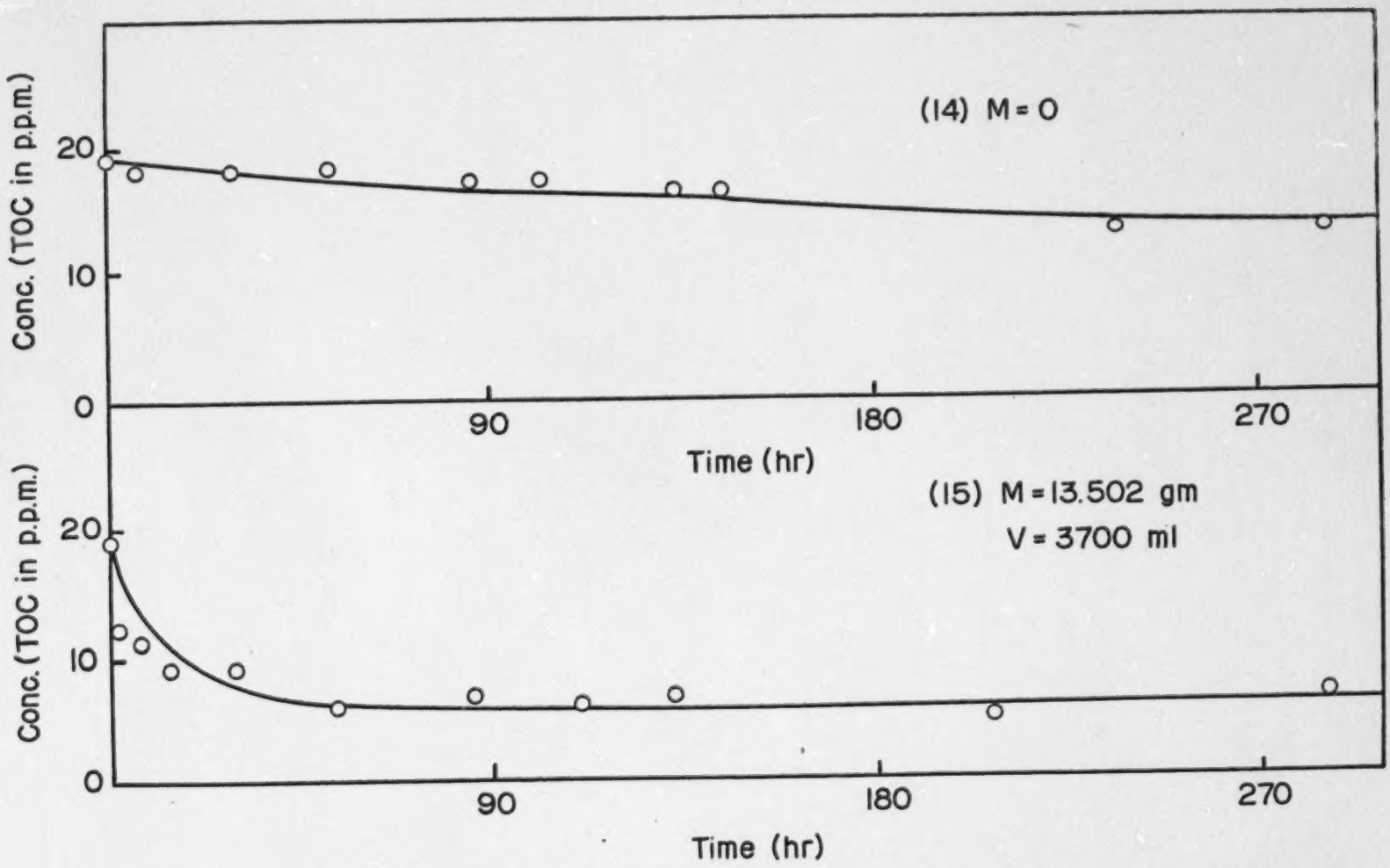

Fig. 10 Batch Adsorption Kinetics Data (e)

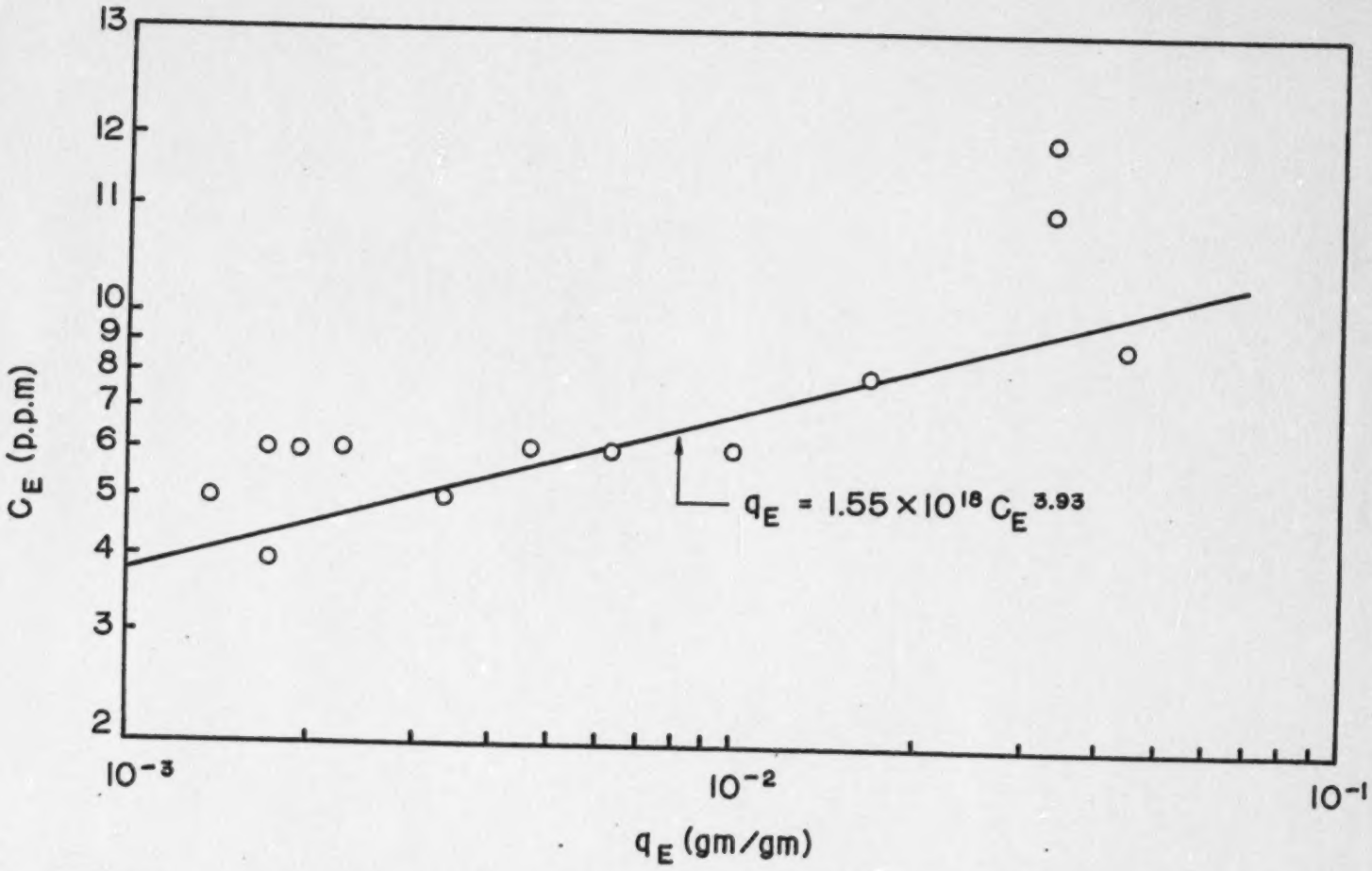

Fig. 11 Adsorption Isotherm Based on Eq. (7) for Decay Rate

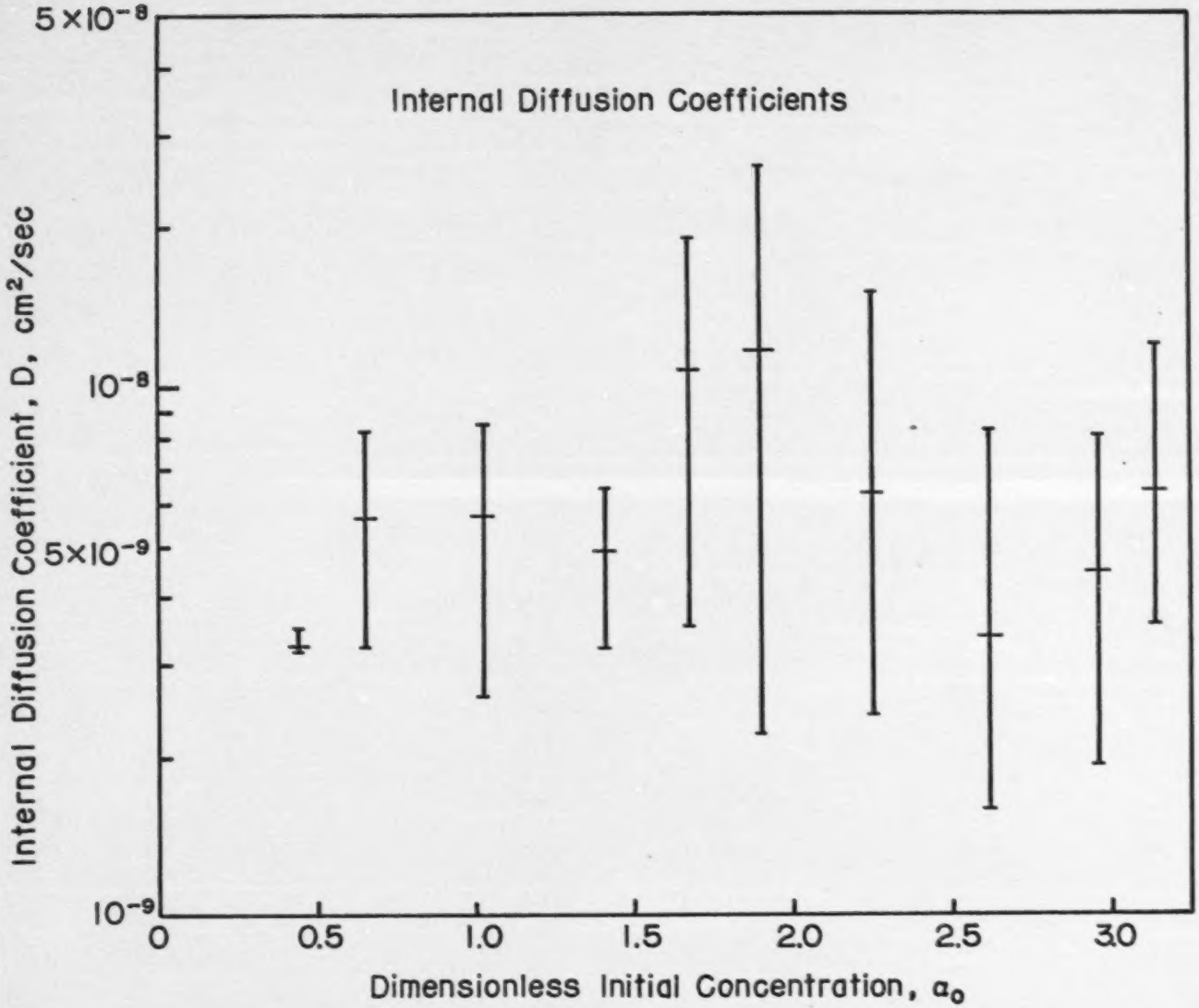

Fig. 12 Scatter of Estimated Internal Diffusion Coefficients

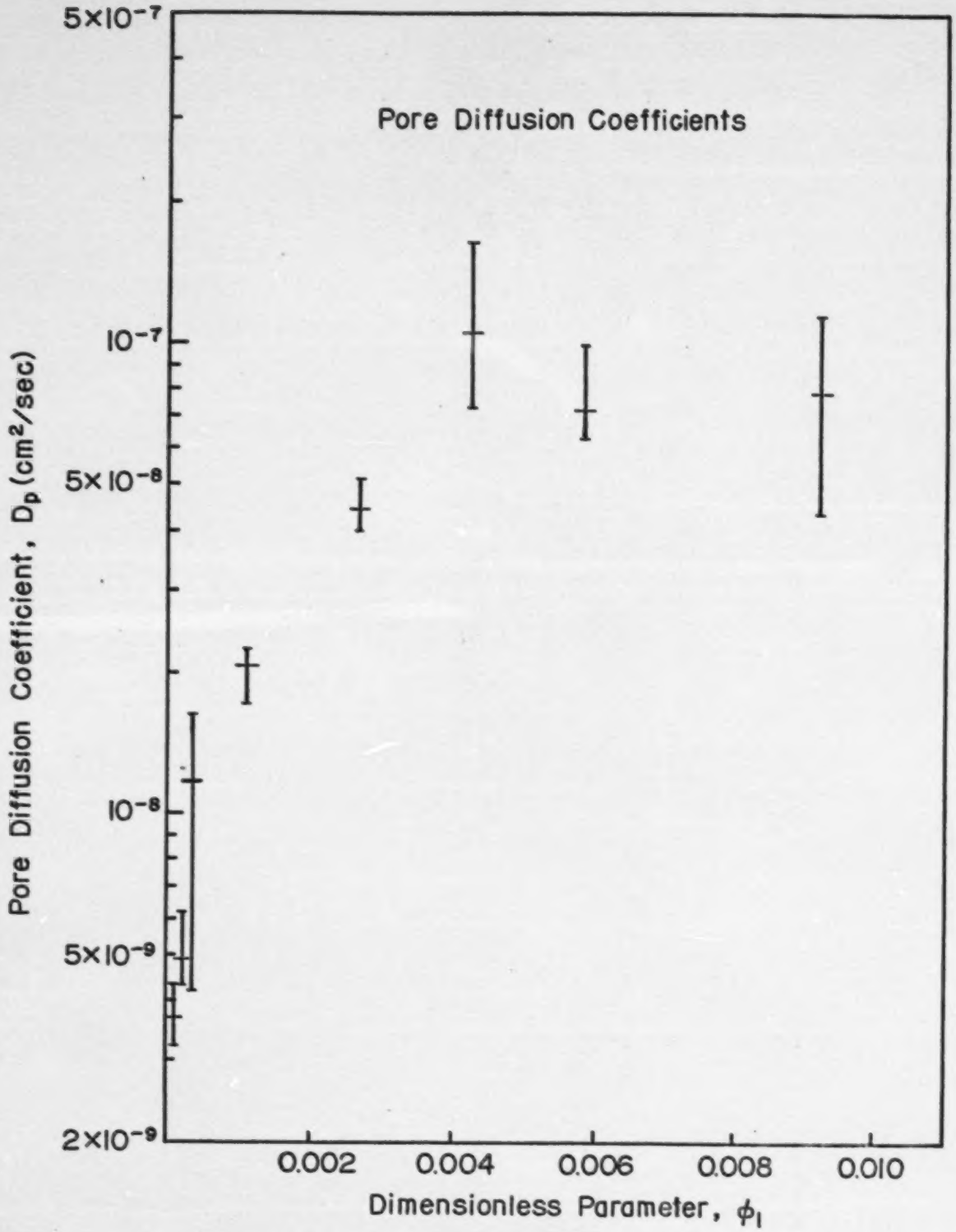

Fig. 13 Scatter of Pore Diffusion Coefficients

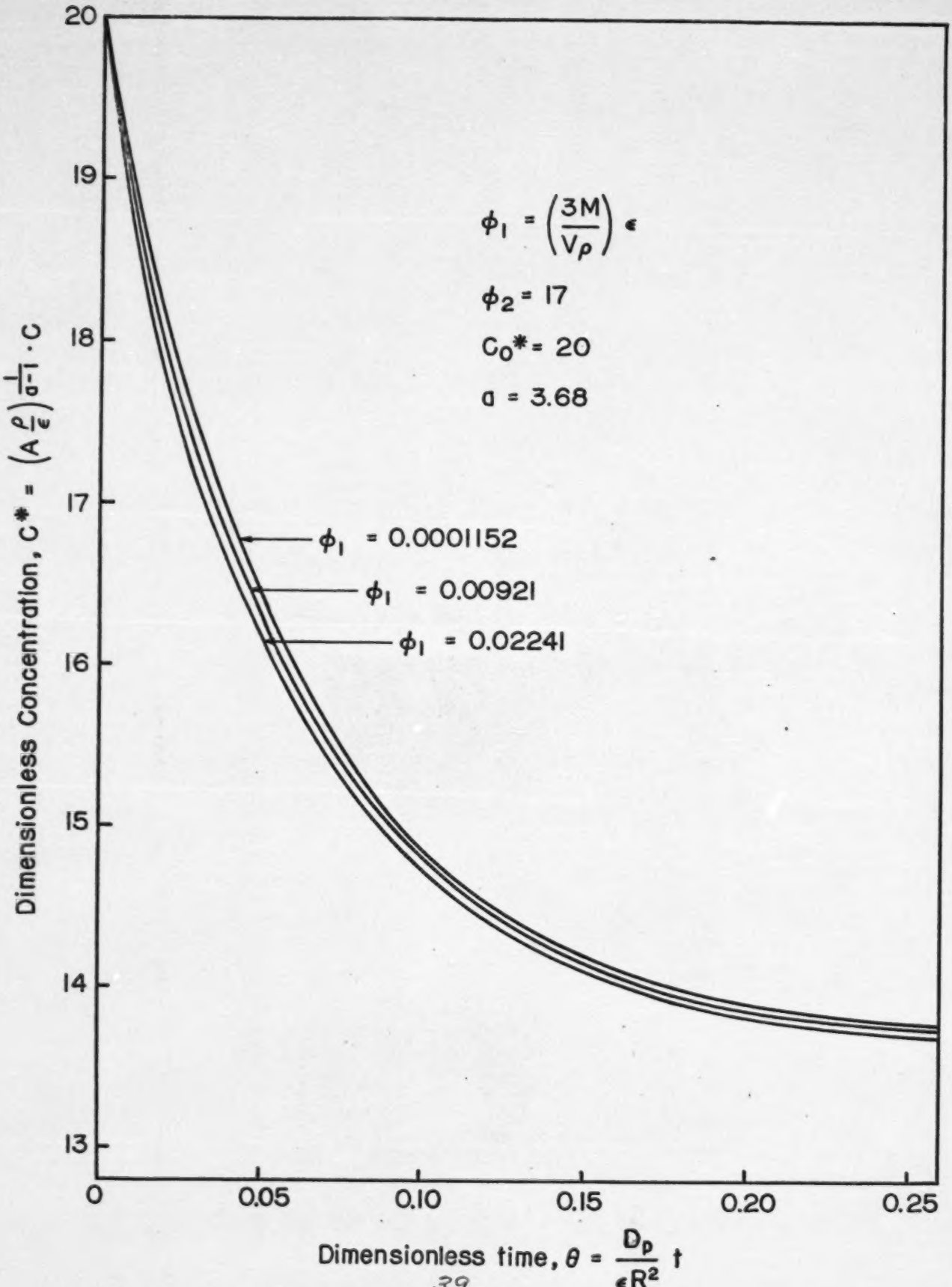

Fig. 14 Theoretical Concentration Histories - Pore Diffusion Model

seems to represent a physically more realistic description of the adsorption process. The theoretical concentration history curve for this model was found to be rather insensitive to the experimental conditions, ϕ_1, (see Figure 14) which makes the error in the pore diffusion coefficient smaller. Despite this apparent advantage, the diffusion coefficient was found to vary over two orders of magnitude (10^{-9} to 10^{-7}).

Wheeler (8) suggested the following relationship between the pore diffusion coefficient, D_p, and the diffusion coefficient of the solute, D_f:

$$D_p = \frac{D_f}{2} \epsilon \qquad (10)$$

in which ϵ is the porosity of the solid. If the contaminants in the waste water were mainly of the ABS type, the pore diffusion coefficient would be of the order of 10^{-8} cm^2/sec. Inasmuch as the contaminants in the waste water we used are not known individually, equation (10) is of limited value.

From the foregoing discussion we conclude, therefore, that based on the results of the present work the adsorption isotherm for the waste water-activated carbon system is of the Freundlich type. Furthermore, the internal diffusion model appears to be a more suitable one than the pore diffusion model in describing the adsorption process, mainly because diffusion coefficients based on this model exhibit relatively smaller variation. The internal diffusion model, in addition, possesses the not too unimportant advantage of leading to relatively simpler mathematical formulations. No doubt the results of experiments on continuous column operation will permit a more effective test of these conclusions. These experiments are being conducted presently in our laboratory.

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NOMENCLATURE

A = coefficient of adsorption isotherm

a = exponent of adsorption isotherm

C = liquid phase concentration

C^* = liquid phase concentration in equilibrium with solid phase concentration q^*

C_{B_E} = quantity appeared in the rate expression (Eq. II-2)

C_o = initial liquid concentration

D = internal diffusion coefficient

D_p = pore diffusion coefficient

k = chemical reaction rate constant

M = amount of adsorbent

q_i = solid phase concentration

q^* = solid phase concentration in equilibrium with liquid phase concentration C^*

q = average solid phase concentration

q_s = solid phase concentration at the adsorbent surface

R = radius of adsorbent

$\bar{R}$ = chemical reaction rate term

t = time

V = volume of liquid

Greek Letters

α = dimensionless concentration defined by Eq. (II-13a)

α_o = initial concentration parameter, defined as $(\frac{MA}{V})^{\frac{1}{a-1}} C_o$

β = dimensionless solid phase concentration, defined by Eq. (II-13b)

δ = parameter defined by Eq. (II-13d)

$\Delta\theta$ = dimensionless time increment

θ = dimensionless time group

APPENDIX I

Calculation of Solid Diffusion Coefficients
Internal Diffusion Model

(1) $M = 0.003$ gm $\quad V = 100$ ml $\quad \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} = 2.31 \times 10^{4}$

$\alpha_o = 0.44 \qquad D = \frac{R^2}{4\pi}\left(\frac{\theta}{t}\right) = 0.00156\left(\frac{\theta}{t}\right)$

$a = 3.68$

t(sec.)	57,600	86,400	108,000	144,000	187,000	237,000	288,000	396,000
C(p.p.m.)	17	16.5	16	15.5	15	14.5	14	13.5
α/α_o*	0.893	0.866	0.841	0.814	0.788	0.761	0.735	0.709
θ*	0.125	0.175	0.23	0.30	0.39	0.52	0.65	0.82
D(cm^2/sec.)	3.4×10^{-9}	3.2×10^{-9}	3.3×10^{-9}	3.2×10^{-9}	3.3×10^{-9}	3.4×10^{-9}	3.5×10^{-9}	3.2×10^{-9}

*See Figure IA

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 3.2 \sim 3.5 \times 10^{-9}$ cm^2/sec.

(3) $M = 0.009$ gm $\quad V = 100$ ml $\quad \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} = 3.48 \times 10^{4}$

$\alpha_o = 0.66 \qquad D = \frac{R}{4\pi}\left(\frac{\theta}{t}\right) = 0.00156\left(\frac{\theta}{t}\right)$

$a = 3.68$

t(sec.)	7,200	10,800	14,400	21,600	28,800	50,400	115,200	194,400
C(p.p.m.)	18	17.5	17	16.5	16	15.5	15	14.5
α/α_o*	0.949	0.923	0.896	0.870	0.844	0.817	0.790	0.765
θ*	0.020	0.041	0.074	0.114	0.160	0.222	0.306	.402
D(cm^2/sec.)	4.3×10^{-9}	5.9×10^{-9}	8.0×10^{-9}	8.2×10^{-9}	8.7×10^{-9}	6.9×10^{-9}	4.1×10^{-9}	3.2×10^{-9}

*See Figure IB

$\delta = KR^2/4\pi D = 2.6 \quad$ (D estimated = 1×10^{-9} cm^2/sec.)

$3.2 \sim 8.77 \times 10^{-9}$ cm^2/sec.

(4) $M = 0.03$ gm $\quad V = 100$ ml $\quad \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} = 5.44 \times 10^{4}$

$\alpha_o = 1.03 \qquad D = \frac{R^2}{4\pi}\left(\frac{\theta}{t}\right) = 0.00156\left(\frac{\theta}{t}\right)$

$a = 3.68$

t(sec.)	10,800	14,400	18,000	25,200	28,800	36,000	50,400	86,400
C(p.p.m.)	17.0	16.5	16	15.5	15	14.5	14	13.5
α/α_o*	0.898	0.871	0.845	0.819	0.792	0.766	0.739	0.713
θ*	0.018	0.030	0.051	0.080	0.124	0.18	0.272	0.416
D(cm^2/sec.)	2.6×10^{-9}	3.2×10^{-9}	4.4×10^{-9}	5.0×10^{-9}	6.7×10^{-9}	7.8×10^{-9}	8.4×10^{-9}	7.5×10^{-9}

*See Figure IA

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 2.6 \sim 8.4 \times 10^{-9}$ cm^2/sec.

(5) $M = 0.07$ gm $\quad V = 100$ ml $\quad \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} = 7.41 \times 10^{4}$

$\alpha_o = 1.41 \qquad D = \frac{R^2}{4\pi}\left(\frac{\theta}{t}\right) = 0.00156\left(\frac{\theta}{t}\right)$

$a = 3.68$

t(sec.)	7,200	10,800	14,400	18,000	25,200	36,000	57,600	108,000
C(p.p.m.)	16	15.5	15	14.5	14	13.5	13	12.5
α/α_o*	0.841	0.815	0.788	0.762	0.736	0.710	0.683	0.657
θ*	0.015	0.022	0.037	0.056	0.088	0.14	0.232	0.40
D(cm^2/sec.)	3.3×10^{-9}	3.2×10^{-9}	4.0×10^{-9}	4.9×10^{-9}	5.5×10^{-9}	6.1×10^{-9}	6.3×10^{-9}	5.8×10^{-9}

*See Figure IB

$\delta = KR^2/4\pi D = 2.6 \quad$ (D estimated $= 1 \times 10^{-9}$)

$D = 3.2 \sim 6.3 \times 10^{-9}$ cm^2/sec.

(6) M = 0.11 gm V = 100 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 8.86 \times 10^4$

$a_o = 1.68$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t})^2 = 0.00156\ (\frac{\theta}{t})$

$a = 3.68$

t(sec.)	7,200	14,400	21,600	28,800	36,000
C(p.p.m.)	15	13.5	12.5	12	11.5
a/a_o*	0.791	0.712	0.659	0.633	0.606
θ*	0.016	0.058	0.16	0.24	0.43
D(cm^2/sec.)	3.5×10^{-9}	6.3×10^{-9}	1.2×10^{-8}	1.3×10^{-8}	1.9×10^{-8}

*See Figure IA

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 3.5 \sim 19 \times 10^{-9}$ cm^2/sec.

(7) M = 0.152 gm V = 100 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 10^5$

$a_o = 1.90$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t}) = 0.00156\ (\frac{\theta}{t})$

$a = 3.68$

t(sec.)	7,200	14,400	21,600	28,800	36,000
C(p.p.m.)	15	13.5	12	11	10.5
a/a_o*	0.789	0.711	0.632	0.579	0.553
θ*	0.010	0.032	0.116	0.340	0.60
D(cm^2/sec.)	2.2×10^{-9}	3.5×10^{-9}	8.4×10^{-9}	1.8×10^{-8}	2.6×10^{-8}

*See Figure IB

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 2.2 \sim 26 \times 10^{-9}$ cm^2/sec.

(8) M = 0.240 gm V = 100 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 1.18 \times 10^5$

$\alpha_o = 2.25$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t}) = 0.00156\ (\frac{\theta}{t})$

a = 3.68

t(sec.)	7,200	14,400	21,600	28,800	36,000
C(p.p.m.)	14	13	11.5	11	10
α/α_o*	0.734	0.682	0.603	0.577	0.524
θ*	0.011	0.022	0.074	0.116	0.336
D(cm^2/sec.)	2.4×10^{-9}	2.4×10^{-9}	5.3×10^{-9}	6.3×10^{-9}	1.5×10^{-8}

*See Figure IA

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 2.4 \sim 15 \times 10^{-9}$ cm^2/sec.

(11) M = 0.516 gm V = 100 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 1.56 \times 10^5$

$\alpha_o = 2.96$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t}) = 0.00156\ (\frac{\theta}{t})$

a = 3.68

t(sec.)	10,800	18,000	28,800	36,000	86,400
C(p.p.m.)	12	11	10	9	8.5
α/α_o*	0.632	0.580	0.527	0.474	0.448
θ*	0.013	0.028	0.066	0.184	0.344
D(cm^2/sec.)	1.9×10^{-9}	2.4×10^{-9}	3.6×10^{-9}	8.0×10^{-9}	6.2×10^{-9}

*See Figure IA

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 1.9 \sim 8.0 \times 10^{-9}$ cm^2/sec.

(12) M = 0.584 gm V = 100 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 1.65 \times 10^5$

$\alpha_o = 3.14$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t}) = 0.00156\ (\frac{\theta}{t})$

a = 3.68

t(sec.)	3,600	7,200	21,600	36,000	57,600
C(p.p.m.)	12	11	10	9	8
α/α_o*	0.631	0.578	0.525	0.473	0.420
θ*	0.012	0.025	0.05	0.128	0.44
D(cm^2/sec.)	5.2×10^{-9}	5.4×10^{-9}	3.6×10^{-9}	5.5×10^{-9}	1.2×10^{-8}

*See Figure IB

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 3.6 \sim 12 \times 10^{-9}$ cm^2/sec.

(15) M = 13.502 gm V = 3700 ml $(\frac{MA}{V})^{\frac{1}{a-1}} = 1.39 \times 10^5$

$\alpha_o = 2.63$ $D = \frac{R^2}{4\pi}(\frac{\theta}{t}) = 0.00156\ (\frac{\theta}{t})$

a = 3.68

t(sec.)	10,800	18,000	28,800	43,200	72,000
C(p.p.m.)	13	12	11	10	9
α/α_o*	0.687	0.634	0.581	0.529	0.476
θ*	0.011	0.022	0.047	0.12	0.38
D(cm^2/sec.)	1.6×10^{-9}	1.9×10^{-9}	2.5×10^{-9}	4.3×10^{-9}	8.2×10^{-9}

*See Figure IB

$\delta = KR^2/4\pi D = 2.6$ (D estimated = 1×10^{-9} cm^2/sec.)

$D = 1.6 \sim 8.2 \times 10^{-9}$ cm^2/sec.

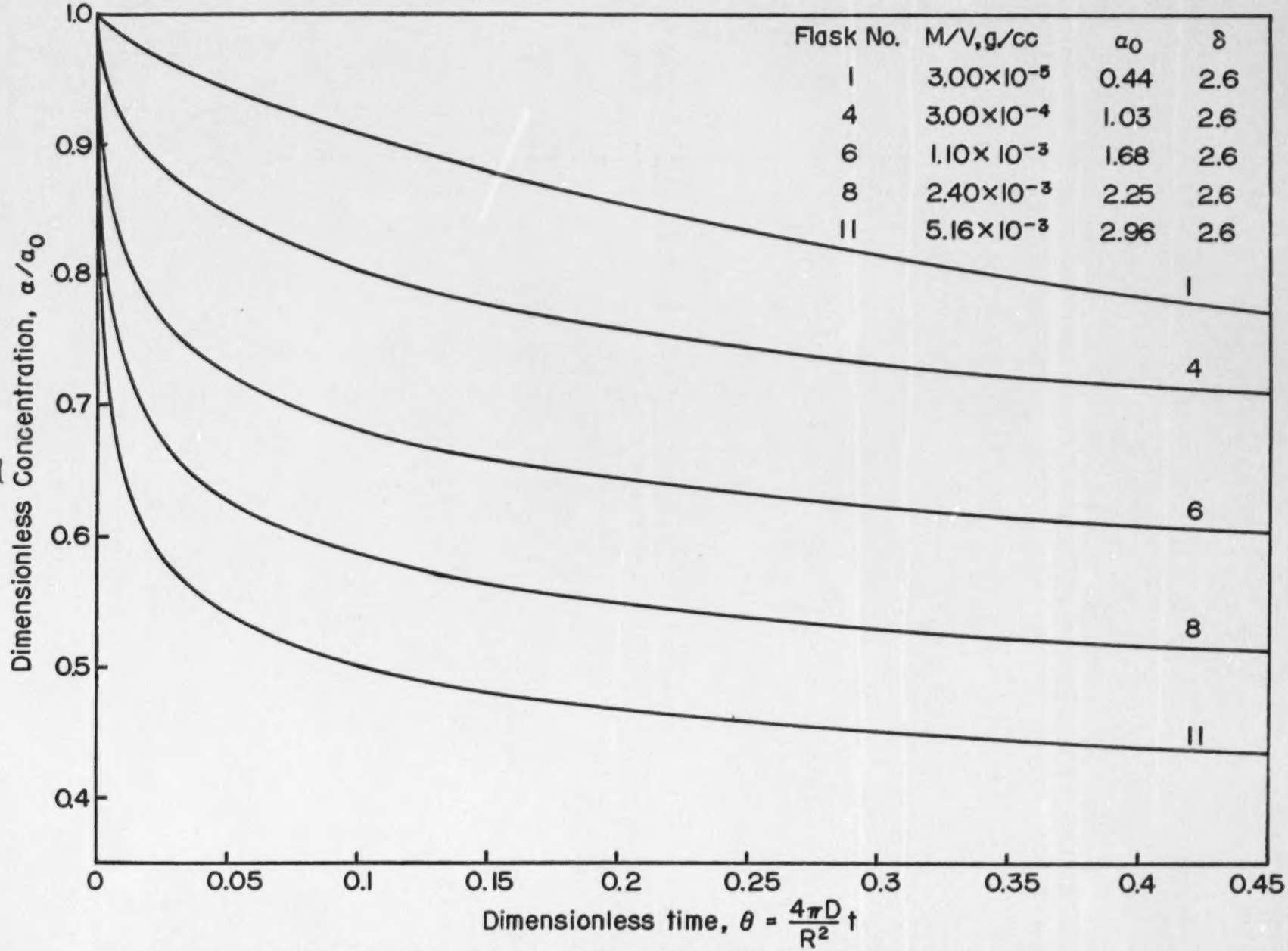

Fig. IA Theoretical TOC Concentration Histories - Internal Diffusion Model

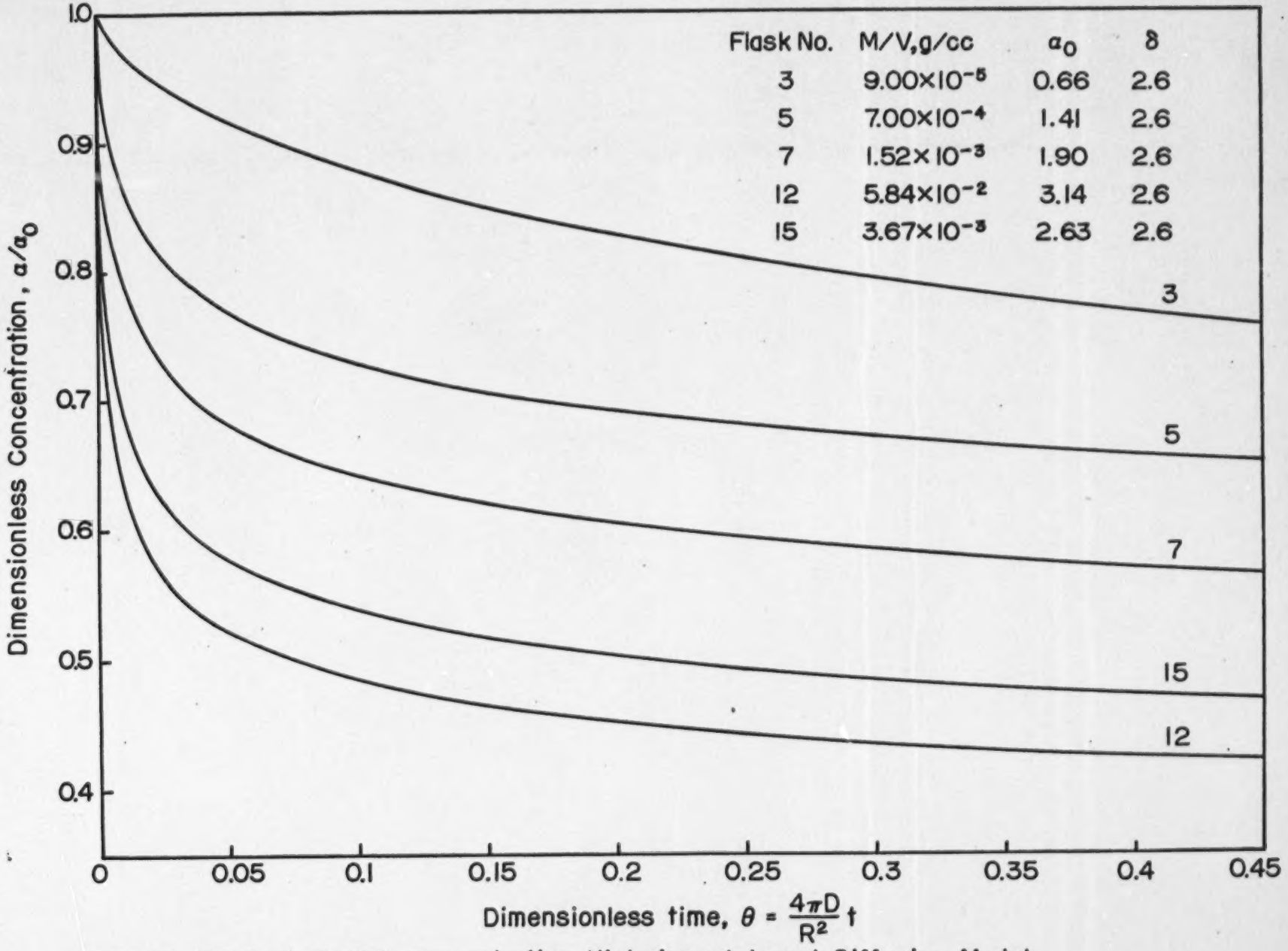

Fig. 1B Theoretical TOC Concentration Histories - Internal Diffusion Model

APPENDIX II

Calculation of Pore Diffusion Coefficients
Pore Diffusion Model

(1) $M = 0.003$ gm $V = 100$ ml $\phi_1 = 0.0001152$

$C_o^* = 20.0$ $\phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	14,400	28,800	43,200	57,600	86,400	108,000
C(p.p.m.)	18.5	18	17.5	17	16.5	16
C*	19.425	18.900	18.375	17.850	17.325	16.800
θ	0.005	0.011	0.017	0.025	0.032	0.042
D_p (cm^2/sec.)	3.4×10^{-9}	3.73×10^{-9}	3.85×10^{-9}	4.25×10^{-9}	3.63×10^{-9}	3.81×10^{-9}

t(sec.)	144,000	187,200	237,600	288,000	396,000
C(p.p.m.)	15.5	15	14.5	14	13.5
C*	16.275	15.750	15.225	14.700	14.175
θ	0.053	0.066	0.084	0.108	0.151
D_p (cm^2/sec.)	3.6×10^{-9}	3.45×10^{-9}	3.46×10^{-9}	3.68×10^{-9}	3.74×10^{-9}

$D_p = 3.4 \sim 4.3 \times 10^{-9}$ cm^2/sec.

(2) $M = 0.006$ gm $V = 100$ ml $\phi_1 = 0.0002304$

$C_o^* = 20.0$ $\phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	21,600	28,800	50,400	72,000	90,000
C(p.p.m.)	18	17.5	17	16.5	16
C*	18.900	18.375	17.850	17.325	16.800
θ	0.011	0.018	0.025	0.033	0.042
D_p(cm^2/sec.)	4.99×10^{-9}	6.13×10^{-9}	4.86×10^{-9}	4.49×10^{-9}	4.57×10^{-9}

t(sec.)	118,800	144,000	180,000	216,000	259,000
C(p.p.m.)	15.5	15	14.5	14	13.5
C*	16.275	15.750	15.225	14.700	14.175
θ	0.052	0.066	0.084	0.108	0.151
D_p(cm^2/sec.)	4.28×10^{-9}	4.49×10^{-9}	4.57×10^{-9}	4.9×10^{-9}	5.7×10^{-9}

$D_p = 4.3 \sim 6.1 \times 10^{-9}$ cm^2/sec.

(3) M = 0.009 gm V = 100 ml $\phi_1 = 0.0003456$

$C_o^* = 20.0$ $\phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	7,200	10,800	14,400	21,600
C(p.p.m.)	18	17.5	17	16.5
C^*	18.900	18.375	17.850	17.325
θ	0.011	0.016	0.024	0.031
$D_p(cm^2/sec.)$	1.50×10^{-8}	1.45×10^{-8}	1.63×10^{-8}	1.41×10^{-8}
t(sec.)	28,800	50,400	115,200	194,400
C(p.p.m.)	16	15.5	15	14.5
C*	16.800	16.275	15.750	15.225
θ	0.041	0.052	0.063	0.083
$D_p(cm^2/sec.)$	1.39×10^{-8}	1.01×10^{-8}	5.36×10^{-9}	4.18×10^{-9}

$D_p = 4.2 \sim 16.3 \times 10^{-9}\ cm^2/sec.$

(4) $M = 0.03$ gm $\quad V = 100$ ml

$$C_o^* = (A\frac{\rho}{\varepsilon})^{\frac{1}{a-1}} \qquad C_o = 1.05 \qquad C_o = 20.0$$

$$\phi_2 = 17 \qquad \phi_1 = 0.001152$$

$$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$$

t(sec.)	10,800	14,400	18,000	25,200	28,800	36,000	50,400	86,400
C(p.p.m.)	17	16.5	16	15.5	15	14.5	14	13.5
C*	17.850	17.325	16.8	16.275	15.750	15.225	14.700	14.175
θ	0.023	0.031	0.041	0.051	0.062	0.082	0.107	0.149
D_p (cm^2/sec.)	2.08×10^{-8}	2.1×10^{-8}	2.23×10^{-8}	1.98×10^{-8}	2.1×10^{-8}	2.23×10^{-8}	2.08×10^{-8}	1.69×10^{-8}

$$D_p = 1.7 \sim 2.2 \times 10^{-8}\ cm^2/sec.$$

(5) M = 0.07 gm V = 100 ml

$C_o^* = (A\frac{\rho}{\varepsilon})^{\frac{1}{a-1}}$ $C_o = 1.05$ $C_o = 20.0$ $\phi_2 = 17$

$\phi_1 = 0.002688$ $D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	10,800	18,000	25,200	36,000	57,600
C(p.p.m.)	15.5	14.5	14	13.5	13
C*	16.275	15.225	14.700	14.175	13.65
θ	0.051	0.081	0.107	0.148	0.30
$D_p(cm^2/sec.)$	4.62×10^{-8}	4.41×10^{-8}	4.16×10^{-8}	4.03×10^{-8}	5.1×10^{-8}

$\therefore D_p = 4.0 \sim 5.1 \times 10^{-8}\ cm^2/sec.$

(6) M = 0.11 gm V = 100 ml

$C_o^* = 20.0$ $\phi_1 = 0.00423$ $\phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	7,200	10,800	14,400	18,000
C(p.p.m.)	15	14	13.5	13
C*	15.750	15.225	14.175	13.65
θ	0.064	0.080	0.146	0.30
$D_p(cm^2/sec.)$	8.7×10^{-8}	7.26×10^{-8}	9.93×10^{-8}	1.63×10^{-7}

$D_p = 7.3 \sim 16.3 \times 10^{-8}\ cm^2/sec.$

(7) $M = 0.152$ gm $\quad V = 100$ ml

$C_o^* = 20.0 \quad \phi_1 = 0.00585 \quad \phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	3,600	7,200	10,800	14,400
C(p.p.m.)	17	16	14.5	13.5
C*	17.850	16.800	15.225	14.175
θ	0.023	0.04	0.081	0.146
D_p (cm^2/sec.)	6.26×10^{-8}	5.45×10^{-8}	7.35×10^{-8}	9.94×10^{-8}

$\therefore D_p = 6.3 \sim 9.9 \times 10^{-8}$ cm^2/sec.

(8) $M = 0.240$ gm $\quad V = 100$ ml

$C_o^* = (A \frac{\rho}{\varepsilon})^{\frac{1}{a-1}} \quad C_o = 20.0$

$\phi_1 = 0.00921 \quad \phi_2 = 17$

$D_p = (\varepsilon R^2)(\frac{\theta}{t}) = 0.0098\ (\frac{\theta}{t})$

t(sec.)	1,800	3,600	5,400	7,200	10,800	12,600
C(p.p.m.)	18	17	16	15	14	13.5
C*	18.900	17.850	16.800	15.750	14.700	14.175
θ	0.008	0.023	0.04	0.064	0.106	0.146
C_p (cm^2/sec.)	4.36×10^{-8}	6.26×10^{-8}	7.26×10^{-8}	8.71×10^{-8}	9.62×10^{-8}	1.14×10^{-7}

$D_p = 4.4 \sim 11.4 \times 10^{-8}$ cm^2/sec.